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CCLXVI.—*The Constitution of Certain Salts and Acids in Solution as determined by Observations of Critical Solution Temperatures.*

By Sydney Raymond Carter and Norman Joseph Lane Megson.

During the course of investigations on the behaviour of sulphur dioxide towards certain salts in acid solutions, the occurrence of complex formation with hydrogen chloride was frequently suspected. Thus, ferric chloride exhibited a far greater tendency than ferrous chloride to combine with hydrogen chloride (J., 1924, **125**, 1886), whilst cupric chloride only appeared to do so at acid concentrations above 7*N* (J., 1925, **127**, 505). Recent work by one of us (this vol., p. 1918) has indicated pronounced combination between hydrogen chloride and mercuric chloride [see also Abegg, "Handbuch der anorganischen Chemie," 1905, II, (2), 641], whilst the reaction between hydrogen chloride and sulphur dioxide or selenium dioxide is much less marked and probably only evident in high concentrations of acid.

It appeared that a study of the mutual miscibilities of liquids, as developed by Pfeiffer (*Z. physikal. Chem.*, 1892, **9**, 444), Timmermanns (*ibid.*, 1907, **58**, 128), and Patterson and his collaborators (*J. Physical Chem.*, 1925, **29**, 295; J., 1925, **127**, 624, 2544; 1926, 2787, 2791) might afford independent confirmation of such complex formation. We wished, however, to work at higher concentrations, if possible, and therefore it was necessary to test the applicability of the method in such cases, since recorded work has hitherto been restricted to the more dilute solutions.

The elevation of the critical solution temperature (*C.S.T.*) of a known mixture produced by each substance was determined separately and then the elevation due to the mixture of the substance with hydrogen chloride was observed. Any decrease from the theoretical elevation was assumed (when not accounted for by other means) to be due to complex formation. Two systems were employed: (1) water and phenol, and (2) water and *iso*butyric acid. The latter system, having a low *C.S.T.*, allows a considerable elevation before the boiling point is reached, and consequently a wide range of concentrations. It also has the advantage that the end-point is more easily determinable than is the case with phenol.

Experimental.

The determination of the *C.S.T.* was carried out in a test-tube fitted with a thermometer and glass stirrer. The apparatus was closed and provision was made for leading in a current of nitrogen

if required. The temperature was controlled by a water-bath and the *C.S.T.* in the case of *iso*butyric acid was observed by the appearance or disappearance of turbidity, as judged with a constant illuminant behind the tube, whilst for phenol, the apparent disappearance of the thermometer bulb was employed, as recommended by Patterson. Readings obtained in this way were reproducible to $\pm 0{\cdot}02°$.

The *iso*butyric acid with water gave a *C.S.T.* of 18·07° over a range of 26·8—28·6% of acid. Since this value is low compared with some of the values in the literature, a small amount of impurity is evidently present, but as this is probably *n*-butyric acid it is not likely to affect the results which follow.

In these results, C is the *molecular* concentration of salt per 1000 g. of total mixture (*i.e.*, water, organic solvent, and solute); e is the elevation of the *C.S.T.* in degrees; and E is the molecular elevation, *i.e.*, $E = e/C$. Table I gives the values of e for given concentrations of the separate constituents in the *iso*butyric acid–water system, as read from smoothed curves.

TABLE I.

C	0·02.	0·04.	0·06.	0·08.	0·10.	0·12.	0·16.	0·20.	0·24.
SeO_2	0·52°	1·00°	1·48°	1·96°	2·40°	2·78°	3·56°	4·30°	5·08°
HCl	2·22	4·00	5·62	7·20	8·62	10·02	12·64	15·20	17·68
$CuCl_2$	5·40	10·28	14·90	19·14	23·00	26·98	33·90	40·22	46·48
$FeCl_2$	5·80	11·04	15·96	20·72	25·14	29·60	38·30	47·10	(55·90)
$FeCl_3$	5·25	10·96	17·60	23·96	30·08	35·76	45·50	(52·90)	—

C	0·30.	0·40.	0·50.	0·60.	0·70.	0·80.	0·90.	1·00.	1·10.
SeO_2	6·24°	8·24°	10·36°	12·80°	14·90°	17·22°	19·60°	21·96°	24·25°
HCl	21·18	26·20	31·50	36·30	40·80	45·10	49·04	52·78	56·20

If these values of e and C be plotted graphically, the curves, with the exception of that of selenium dioxide, deviate from straight lines, giving a curvature which is concave towards the concentration axis. This is in accordance with the decreased ionisation to be expected at the higher concentrations.

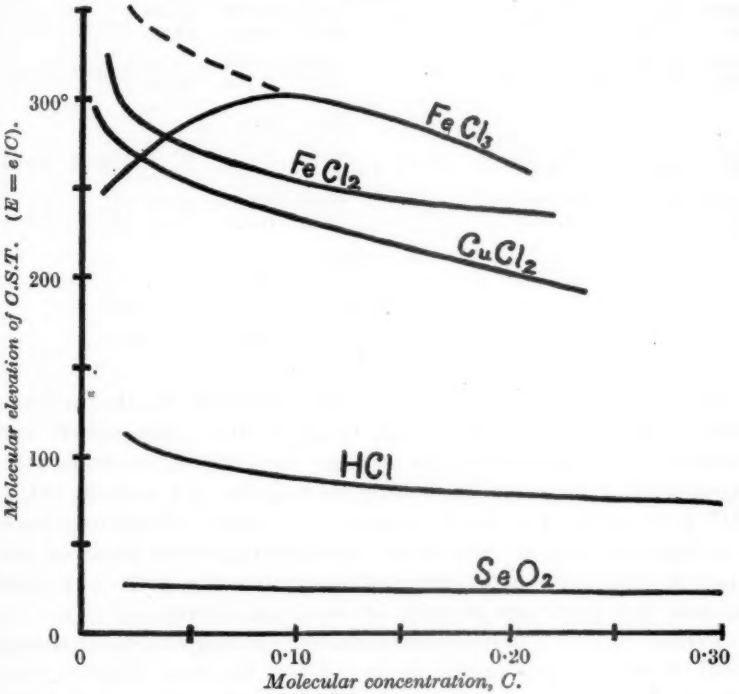
Ferric chloride gives a curvature near the origin which is slightly different from the remainder. These effects are much more clearly shown by plotting E against C (see Fig. 1).

For a normal substance such as hydrogen chloride, E increases with diminishing concentration as the result of ionisation. In the case of ferric chloride the increase ceases at $C = 0{\cdot}09$ and E falls rapidly with further dilution. Since hydrolysis begins to be appreciable at about the same stage, it probably affords an explanation (Goodwin, *Z. physikal. Chem.*, 1896, **21**, 15).

An interesting series of curves is obtained by plotting log e against log C. They approximate to parallel straight lines over a fair

range of concentration, the exception being that of ferric chloride, which crosses those of cupric and ferrous chlorides. The straight lines are in accordance with the equation $\log e = m \log C + b$, which gives the relation $e = AC^m$, proposed by Carrington, Hickson, and Patterson (J., 1925, **127**, 2548). The numerical value of the constant in our case gives $m = 0{\cdot}92$ for the system *iso*butyric acid–water, whilst the previous authors obtained $m = 0{\cdot}84$—$0{\cdot}87$ for phenol–water.

FIG. 1.



The regularity of the results obtained on plotting C against e and E, and $\log C$ against $\log e$, as well as of the results for the mixtures still to be described, suggests that the principles developed by Patterson in the more dilute solutions are also valid for the higher concentrations.

Mixtures of Salts with Hydrogen Chloride.

The possibility of complex formation was investigated, the concentration of the salt being kept approximately constant whilst that of the hydrogen chloride was varied over a fairly wide range. The theoretical elevation of the *C.S.T.*, denoted by "Mean e calc.,"

is half the sum of the elevations for *double* the concentration of each constituent, as described by Patterson (J., 1925, **127**, 626). This rule can be applied when the values of e for the salt and hydrogen chloride do not vary considerably, but for differences greater than 20° it is not so accurate.

TABLE II.

$SeO_2 + HCl$.					$CuCl_2 + HCl$.				
	C.	*e* calc.	Mean *e* calc.	*e* obs.		*C.*	*e* calc.	Mean *e* calc.	*e* obs.
SeO_2	0·681	30·58°	39·70°	39·63°	$CuCl_2$	0·103	41·20°	36·42°	36·75°
HCl	0·438	48·80			HCl	0·241	31·65		
SeO_2	0·347	14·78	26·66	27·87	$CuCl_2$	0·090	37·20	30·47	30·83
HCl	0·312	38·54			HCl	0·168	23·75		
$FeCl_2 + HCl$.									
$FeCl_2$	0·105	48·95	33·30	33·60	$FeCl_2$	0·0716	35·20	36·65	36·29
HCl	0·116	17·65			HCl	0·307	38·10		
$FeCl_2$	0·0703	34·60	31·20	31·08	$FeCl_2$	0·0681	33·80	26·49	26·47
HCl	0·205	27·80			HCl	0·128	19·81		

$SO_2 + HCl$.

	C.	*e* calc.	Mean *e* calc.	*e* obs.
SO_2	(0·4)	5·0°	33·0°	34·2°
HCl	0·550	61·0		

No consistent lowering of e is thus observed for the mixtures $SeO_2 + HCl$, $FeCl_2 + HCl$, and $CuCl_2 + HCl$. The actual concentration of sulphur dioxide was not determined, since the same stock solution was used in making up both the SO_2 and the $SO_2 + HCl$ mixtures for the determination of e. Only a slight increase in e is observed, and in view of the experimental errors involved, this may be interpreted as evidence of no combination between sulphur dioxide and hydrogen chloride at these concentrations.

Ferric Chloride and Hydrogen Chloride.—It was evident that some kind of reaction was taking place. When the ferric chloride alone was in the mixture of *iso*butyric acid and water, it imparted a dark brown colour to the organic layer. On addition of hydrogen chloride, this became lighter, assuming a light yellow colour when the ratio $HCl : FeCl_3$ reached 6 : 1. The concentration of ferric chloride was kept at *ca.* 0·08 whilst that of hydrogen chloride was varied from 0·08 to 0·50, and in these circumstances depressions of e were observed as shown in Table III.

The consistent appreciable decrease in e is evidence of complex formation, and since the greatest percentage decrease occurs when $HCl : FeCl_3 = 3 : 1$, it appears probable that the compound $FeCl_3,3HCl$ exists in solution.

The complex ferric compounds which are formed by carboxylic

TABLE III.

C.		*e* calc.					
$FeCl_3$.	HCl.	$FeCl_3$.	HCl.	Mean *e* calc.	*e* obs.	Diff.	Decrease in *e*, %.
0·0766	0·0790	43·65°	13·00°	28·33°	29·36°	+1·03°	—
0·0824	0·1715	46·42	27·40	34·91	33·33	−1·58	4·6
0·0836	0·2446	46·80	31·42	39·11	36·63	−2·48	6·5
0·0844	0·2625	47·20	32·72	39·96	37·08	−2·88	7·5
0·0869	0·2770	48·20	34·10	41·15	37·98	−3·17	8·0
0·0815	0·3145	46·10	37·65	41·87	39·77	−2·10	5·1
0·0764	0·4370	44·00	48·10	46·05	43·51	−2·54	5·7

acids, such as acetic acid, might be expected to explain the anomalous behaviour of ferric chloride in *iso*butyric acid :

$$3FeCl_3 + 6CH_3{\cdot}CO_2H + 2H_2O \rightleftharpoons [Fe_3(OH)_2(CH_3{\cdot}CO_2{\cdot})_6]Cl + 8HCl$$

(Weinland, " Complex-Verbindungen," 1919, pp. 345 *et seq.*). The brown coloration may then be satisfactorily attributed to the coloured complex, whilst the subsequent addition of hydrochloric acid leads to the repression of complex formation and a consequent fading of colour.

The occurrence of complex formation causes solubility of the ferric chloride in both liquids instead of in the water alone, and this would tend to decrease the *C.S.T.*, especially for higher concentrations of ferric chloride. Since, however, the abnormalities in *C.S.T.* are mainly observed at the lower concentrations of ferric chloride, and in the opposite sense, we consider that the extent of interaction between the ferric chloride and *iso*butyric acid must be relatively small.

For the remaining examples, the phenol–water system was found more convenient.

Mercuric Chloride and Hydrogen Chloride.—Mercuric chloride is soluble both in phenol and in *iso*butyric acid, but the former solvent was found to be more suitable to work with. The *C.S.T.* was depressed and *e* was negative (Table IV).

TABLE IV.

C	0·05	0·10	0·15	0·20	0·25
$-e$ for $HgCl_2$	1·72°	3·58°	5·58°	7·72°	9·85°
$+e$ for HCl.....	3·58	6·50	9·02	11·38	13·60
C	0·30	0·35	0·40	0·50	0·60
$-e$ for $HgCl_2$	12·00°	14·10°	—	—	—
$+e$ for HCl.....	15·80	17·50	19·18	22·20	(24·7)

The graph of log *C* against log *e* for mercuric chloride is a straight line and its slope indicates $m = 1{\cdot}1$. This differs from the normal value, 0·87, for ordinary substances insoluble in phenol.

The concentration of mercuric chloride was kept nearly constant and that of hydrogen chloride varied; the results obtained are given in Table V, and afford an example of the *C.S.T.* being raised by a

TABLE V.

C_{HgCl_2}.	C_{HCl}.	Mean e calc.	e obs.	Increase.
0·248	0·108	−4·2°	− 3·5°	0·7°
0·243	0·168	−1·5	+ 0·1	1·6
0·245	0·250	+1·05	+ 4·79	3·74
0·249	0·278	+1·55	+ 6·81	5·26
0·244	0·456	+6·20	+15·20	9·0
0·244	0·479	+6·65	+15·84	9·2
0·226	0·595	+9·75	+21·66	11·9

mixture. It is raised to an extent greater than would be expected from the simple mixture, and the effect increases with relative increase in the ratio $HCl/HgCl_2$. Since one of the constituents, mercuric chloride, is soluble in the phenol layer, it shows that a complex is being formed which is insoluble in phenol.

Cuprous Chloride and Hydrogen Chloride.—The value "Mean e calc." = (25°) is an approximation and indicates a lower limit, since "e calc." has been estimated by analogy with the chlorides of univalent metals. If cuprous copper exerts a higher valency as in the double formula Cu_2Cl_2 a still higher value would result. In either case, the low value of e obs. is thus in accordance with complex formation.

(Phenol–water system.)

	C.	e calc.	Mean e calc.	e obs.
HCl	0·422	35°	(25°)	22·2°
CuCl	0·0836	(15)		

Summary.

The elevation of critical solution temperature has been employed in order to study complex formation in hydrogen chloride solutions.

The values of e for various salts and acids have been determined in the system *iso*butyric acid–water, and for mercuric chloride in the phenol–water system.

Values of e and E obtained for these salts are regular, except in the case of ferric chloride, in which hydrolysis probably occurs.

The constant m approximates to 0·92 in the equation $e = AC^m$ for *iso*butyric acid–water.

No complex formation has been found between hydrogen chloride and sulphur dioxide, selenium dioxide, or ferrous and cupric chlorides, but considerable complex formation occurs between hydrogen chloride and ferric, mercuric, or cuprous chloride in the concentrations used.

The concentrations are considerably higher than those used hitherto, but the principles are still applicable.

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EDGBASTON.

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CCLXVII.—*The Electronic Structure of Atoms. Part I. The Periodic Classification.*

By J. D. MAIN SMITH.

THE outstanding feature of theories of the structure of atoms is their extensive and intimate relationship to the facts of chemistry summarised in the periodic classification of the elements. This relationship consists essentially in referring the periodicity in the properties of elements to a corresponding periodicity in the structural complexity of their atoms. The existence of this correspondence is readily deducible from a multitude of correlated chemical and physical experimental facts, but its precise nature has been variously interpreted, and diverging views have consequently been held as to the electronic structures attributable to the atoms of the elements.

Examination of the arrangement of the elements in the order of atomic weight shows that characteristic types of elements recur at fixed intervals or periods. The number of elements intervening in a period is always 8, 18, or 32. For example, if the noble gases be taken as points of reference, there are 8 elements from helium to neon and from neon to argon, 18 from argon to krypton and from krypton to xenon, and 32 from xenon to radon.

These sets of elements constitute Mendeléev's periods (see Table 1), the first two sets of 8 elements forming the first two "short"

TABLE 1.

Periodic Classification.

Group. Valency.	I. +1	II. +2	III. +3	IV. +4 −4	V. +5 −3	VI. +6 −2	VII. +7 −1	VIII. Zero or +8
Period.								
1	1H						(1H)	2He
2	3Li	4Be	5B	6C	7N	8O	9F	10Ne
3	11Na	12Mg	13Al	14Si	15P	16S	17Cl	18A
4	19K 29Cu	20Ca 30Zn	21Sc 31Ga	22Ti 32Ge	23V 33As	24Cr 34Se	25Mn 35Br	26Fe,27Co,28Ni,(Cu,Zn) 36Kr
5	37Rb 47Ag	38Sr 48Cd	39Y 49In	40Zr 50Sn	41Cb 51Sb	42Mo 52Te	43Ma 53I	44Ru,45Rh,46Pd,(Ag,Cd) 54Xe
6	55Cs 79Au	56Ba 80Hg	57La+ * 14 "Rare Earths" 81Tl	72Ct 82Pb	73Ta 83Bi	74W 84Po	75Re 85—	76Os,77Ir,78Pt,(Au,Hg) 86Rn
7	87— —	88Ra	89Ac	90Th	91Pa	92U		

* 58Ce, 59Pr, 60Nd, 61Il, 62Sm, 63Eu, 64Gd, 65Tb, 66Dy, 67Ho, 68Er, 69Tm, 70Yb, 71Lu

periods, and the remaining sets of more than eight elements forming the "long" periods. The first two long periods of 18 elements fall into two series of eight valency groups, the "even" series consisting of 10 elements (three in Group VIII), and the "odd"

series of 8 elements. The third long period, containing 32 elements, has been a subject of much discussion, but it is now generally agreed that it is divisible into two series or sub-periods like the other long periods, the even series, however, being of 24 elements, from cæsium to platinum, and the odd series as before of eight elements, from gold to the noble gas radon. It is assumed that in this period only one element, eka-iodine, belonging to the halogen group, remains to be discovered.

The Abridged Periodic Classification.

The history of chemical science has demonstrated clearly that the most useful method for the condensation and generalisation of data is that of classification by types. In organic chemistry, the method proceeds according to constitutional types, such as alcohols, ketones, aldehydes, etc., by reference to *structural* features possessed in common by *compounds*. In inorganic and general chemistry, the method proceeds similarly according to constitutional types, by reference to *valency* features possessed in common by *atoms*. The periodic classification is essentially classification by valency types, the elements being arranged into eight groups having valency from one to eight respectively. This supremely important octet classification is somewhat obscured by the detail introduced by the division of the long periods into the unequal sub-periods of the even and odd series. Modifications intended to simplify and increase the chemical utility of the classification must emphasise this octet arrangement. Many of those proposed in recent years, however, have had for their object, not the increase in the chemical utility of classification of detailed knowledge, but the facilitation of mathematical interpretations of atomic structure, and with this in view the number of groups is successively increased from 8 to 18 and 32 in passing from the short to the long periods. In all such systems, the essential chemical features of classification by valency and periodicity of properties are subordinated or suppressed, although the structure of atoms is fundamentally a chemical problem, profoundly interwoven with the periodic classification of the elements. It will be shown that abridgment, rather than expansion, clarifies the classification, and facilitates a more intimate and accurate interpretation of atomic structures, by throwing the chemically important octet arrangement into high relief.

In the classification of the elements by valency types, the 16 light elements from lithium to argon fall naturally into two periods of eight groups with one element per group per period, each period ending with a noble gas. These two periods may, consequently, be regarded as simple or specific types for the heavier elements of

the long periods. Consideration of the properties of these heavier elements shows that, in each long period, only a few elements approximate closely in properties to the simple types of the short

TABLE 2.

Abridged Periodic Classification.

Class.	Alkaline.		Amphoteric.		Non-Basic.			
Group.	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
Valency.	+1	+2	+3	+4 −4	+5 −3	+6 −2	+7 −1	Zero
Period.								
1	1H						(1H)	2He
2	3Li	4Be	5B	6C	7N	8O	9F	10Ne
3	11Na	12Mg	13Al	14Si	15P	16S	17Cl	18A
4	19K	20Ca*	31Ga	32Ge	33As	34Se	35Br	36Kr
5	37Rb	38Sr†	49In	50Sn	51Sb	52Te	53I	54Xe
6	55Cs	56Ba‡	81Tl	82Pb	83Bi	84Po	85—	86Rn
7	87—	88Ra§						

* 10 Elements, 21Sc to 30Zn
† 10 Elements, 39Y to 48Cd
‡ 24 Elements, 57La to 80Hg
§ All elements from 89Ac
} relegated to Table 3.

periods, and that in any one period some of these kindred elements appear in the even and some in the odd series. Mendeléev suggested that the elements diverging most from the specific types were in the nature of " transition " elements bridging a gap between the typical elements of each long period, a view adopted later in a modified form by Bohr in his theory of atomic structure. Mendeléev's suggestion is virtually a recognition that the long periods can be short-circuited by excluding the transition elements, leaving an abridged classification constituted solely of elements closely related to the short period types, the periodic classification thus consisting only of simple periods each of eight elements.

In order to effect this short-circuiting or abridgment of the long periods, it is necessary to decide which elements are most closely related to the typical elements of the short periods, the remaining elements being relegated to transition series. In the first long period (see Table 1), it is evident that potassium and the elements from gallium to krypton are more closely related to sodium and the elements from aluminium to argon than are copper and the elements from scandium to nickel, and these last nine elements are therefore definitely transition elements. There remain only calcium and zinc for consideration. As one of the obvious features of the periodic classification is the increase in basicity with increase in atomic weight in each group, the element corresponding to magnesium, the oxide of which is feebly alkaline, should possess a strongly alkaline oxide, the heavier members of the group having still more alkaline

oxides. This circumstance involves that the congeners of beryllium and magnesium are the alkaline-earth metals, calcium, strontium, barium and radium, whilst zinc, cadmium, and mercury are transition elements.

The transition elements of the first long period are consequently the ten elements from scandium to zinc (see Table 3). The remaining eight elements, potassium, calcium, and gallium to krypton, form an abridged period (see Table 2) with one element per periodic group, exhibiting extremely close resemblance to the typical elements of the short periods. Similar considerations apply to the second long period, the transition elements being the ten from yttrium to cadmium (see Table 3). The remaining eight elements, rubidium, strontium, and indium to xenon, form an abridged period with one element per periodic group. In the third long period, consisting of 32 elements, it is similarly possible to allocate the eight elements cæsium, barium, and thallium to radon to the abridged period. The 24 elements from lanthanum to mercury are in consequence relegated to the transition series.

In the fourth long period, the known elements come to an end with uranium in Group VI of the even series. The chemical and physical properties of actinium, thorium, protactinium, and uranium indicate decisively that they are analogues of yttrium, zirconium, etc., and therefore transition elements. The only remaining known element of the period is radium, which resembles barium so closely that it can be separated from it only with difficulty. Radium consequently is an alkaline-earth metal and must be regarded, not as a transition element, but as the Group II representative in the abridged classification. Similarly, eka-cæsium must, as an alkali metal, be postulated as the Group I representative of the abridged classification, not as a transition element. The existence of only one element, actinium, between thorium and radium renders it certain that the transition series of this last long period contains no transition sub-series similar to the anomalous 14 "rare-earth" elements (see p. 2035), and it is consequently probable that, if all the elements of this period were known, they would number only 18 as in the case of the first and second long periods.

There remain for consideration only the two lightest elements, hydrogen and helium. Apart from hydrogen, no element lighter than helium is known, and many considerations, chemical and physical, render it improbable that any other element can exist. If it be admitted that electrons are the sole valency factors, the fact that helium contains only two electrons makes it certain that hydrogen with one electron is the only possible element lighter than helium. Despite the validity and utility of the octet classification,

it is thus impossible to fill more than two of the eight groups of this primitive period. As the unit of valency and of atomic weight, hydrogen may be regarded as the type of all the valent elements and placed at the head of any of the Groups I to VII of the classification, helium being placed at the head of Group VIII as the type of all the non-valent and noble elements. It is not a matter of importance, in the classification of the elements, in which group hydrogen is placed, but from its univalency it may conveniently be placed in Group I *and* alternatively in Group VII.

The modification of the periodic classification derived from the foregoing considerations is shown in Table 2, and consists of a primitive period of two elements, two short periods each of eight elements, three abridged long periods each of eight elements, and a final abridged and incomplete period, or seven periods in all. Examination of these seven abridged periods reveals much greater regularities in the classification than are readily discernible in the extended form. Basicity, for example, *diminishes* regularly in each *period* from strong alkalinity in the first group to strong acidity in the seventh, and *increases* regularly in each *group* from the first to the seventh period. Further, all the elements which possess alkaline oxides are confined to Groups I and II. The alkaline thallous and plumbous oxides are only apparent exceptions to this rule, for in neither case does the metal exhibit the valency characteristic of the periodic group to which it belongs. This disappearance of alkalinity beyond Group II is of fundamental importance in the interpretation of the electronic structures of the atoms of all the elements, in Groups III to VIII no less than in Groups I and II, for, being a measure of electron mobility, it enables a differentiation to be made amongst the various sub-groups of electrons that constitute the exterior of atoms.

Comparison of Groups III and IV with Groups V, VI, and VII brings to light a further regularity relating to basicity. The whole of the elements of Groups III and IV possess amphoteric oxides, their basic tendencies being approximately equal to their acidic tendencies, and, where the elements exhibit lower valency, the lower oxides are never amphoteric but decidedly basic or even alkaline, as in the case of thallous and plumbous oxides. In Groups V to VIII, on the other hand, all the elements yield oxides which are strongly acidic, and, even where the basic properties are in any degree exhibited by the oxides, as in the case of bismuth and antimony, the derived salts are without exception hydrolysed by water to basic salts. Further, where the elements of Groups V to VII exhibit lower valency than that characteristic of the group, even the lower oxides are usually strongly acidic. Groups V to

VIII, moreover, include every known element which is gaseous below a red heat. The elements of Groups III and IV are consequently as sharply differentiated from those of Groups V to VII as from those of Groups I and II. The periodic classification can thus be divided, not only into groups, periods, and even, odd, and transition series, but also into classes of groups; the first class, Groups I and II, contains what may be termed the alkaline elements; the second class, Groups III and IV, the amphoteric elements; and the third class, Groups V, VI, VII, and VIII, the non-basic elements.

Variable Valency.

A further noteworthy feature of the abridged classification is that, without exception, every element exhibiting variable valency possesses valencies which differ by only 2, 4, or 6 units, iodine, for example, having valencies of 7, 5, 3, and 1. Apparent exceptions to this rule may be found in the case of gallium and indium : both metals, though normally tervalent, are stated to yield bivalent salts, while indium is stated to yield univalent salts in addition. The vapour density of indium " dichloride " slightly above its boiling point, however, proves the formula to be In_2Cl_4, not $InCl_2$. The dichloride has therefore no real existence, and it may be regarded as a double salt of the monochloride and trichloride, $InCl,InCl_3$ or $In(InCl_4)$. Gallium " dichloride " boils at 535°, but its vapour density has been recorded only at 1000° where it is normal. If, however, the formula is Ga_2Cl_4 and dissociation occurs on heating to a mixture of GaCl and $GaCl_3$, the vapour density of the mixture will be the same as that of $GaCl_2$. Fused gallium trichloride is a non-electrolyte, like aluminium chloride, whereas the alleged dichloride is a good conductor and readily yields metallic gallium on electrolysis, pointing to the formula $Ga(GaCl_4)$ or Ga_2Cl_4. A similar dimeric " dichloride " is obtained from thallium by mixing the monochloride with the trichloride, and it is definitely known that thallium does not exhibit bivalency. If gallium and indium " dichlorides " are, as suggested, really gallous gallichloride and indous indichloride, respectively, these two metals fall into line with thallium in the same group as possessing only tervalency and univalency, and the apparent exceptions to the rule of variation by two units of valency disappear from the abridged classification.

The Transition Series.

It has been shown, in connexion with the abridgment of the periodic classification, that 10 elements in each of the first two long periods, 24 in the third long period, and four of the six known elements of the last period show very considerable divergence from

the properties of the typical elements of the two short periods, and are to be regarded as transition elements bridging a gap in each long period between elements most closely allied to the typical elements. In the first long period, these ten transition elements, from scandium to zinc, may be arranged in a sub-period or transition series consisting, like the abridged periods, of eight valency groups (see Table 3). The lightest member of the series, scandium, with an

TABLE 3.

All Transition Series.

Group.	III.	IV.	V.	VI.	VII.	VIII.			I.	II.
Valency.	+3 to 2	+4 to 2	+5 to 2	+6 to 2	+7 to 2	+8 to Zero			+1 to 3	+2 to 1
Period.										
4	21Sc	22Ti	23V	24Cr	25Mn	26Fe	27Co	28Ni	29Cu	30Zn
5	39Y	40Zr	41Cb	42Mo	43Ma	44Ru	45Rh	46Pd	47Ag	48Cd
6	57La*	72Ct	73Ta	74W	75Re	76Os	77Ir	78Pt	79Au	80Hg
7	89Ac	90Th	91Pa	92U						

* 14 Elements, 58Ce to 71Lu, relegated to Table 4.

invariable valency of three, naturally falls into Group III, the heaviest member, zinc, with an invariable valency of two, being proper to Group II, the transition period thus commencing with Group III and ending with Group II.

The set of ten transition elements from the second long period correspond so closely in chemical and physical properties to the ten transition elements from the first long period that, without further discussion, they may be allocated to the corresponding eight groups from III to II (see Table 3).

Owing to the fact that there are 24 transition elements in the third long period as against 10 in the other two long periods, no complete analogy exists, but the nine elements from celtium (hafnium) to mercury in this longest transition series present so close a resemblance to the nine elements in the preceding transition series, from zirconium to cadmium, that they may readily be allocated to the seven corresponding periodic groups from IV to II. There remain in this transition series only the 15 elements having atomic weights lying between barium in Group II and celtium (hafnium) in Group IV. These elements from lanthanum to lutecium (known as " rare-earth " elements) have characteristic tervalency, are relatively strong bases, and give rise to basic salts of the type $La(OH)CO_3$, and mixed salts of the type $LaFCO_3$. There can, therefore, be no doubt that these elements are completely analogous to yttrium and scandium, and are proper to Group III. This transition series of 24 elements may be short-circuited or abridged (see Table 3) by the omission of 14 of the 15 " rare-earth " elements in Group III, leaving an abridged transition series of 10

elements corresponding closely in every member to each of the transition series from the first two long periods. It is not a matter of great importance chemically which 14 "rare-earth" elements are relegated to a transition sub-series, but the relegation is of prime importance in the problem of the electronic structures of the atoms of this period. It is consequently necessary to make a decision, on chemical grounds if possible, as to the element presenting the closest resemblance to yttrium and scandium in the two preceding transition series, and to place the other fourteen in a transition sub-series. Scandium and yttrium have no valency higher than three, whilst yttrium (certainly) and scandium (probably) exhibit the valency of two in acetylenic carbides of the form YC_2. Both yield colourless, diamagnetic salts, while yttrium oxide is a stronger base than scandium oxide, the basicity of the former only just falling short of alkalinity. Consequently the element to be placed in Group III of the third transition series should have no higher valency than three, exhibit a valency of two in an acetylenic carbide, and possess colourless, diamagnetic salts and a strongly alkaline oxide. These properties are possessed only by the lightest of these elements, lanthanum, which must, accordingly, be regarded as the Group III representative in the transition series of the third long period, the remaining 14 from cerium to lutecium, being relegated to a transition sub-series (see Table 4). This transition sub-series

TABLE 4.

Transition Sub-series, Period 6.

Element.	Ce	Pr	Nd	Il	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
	58	59	60	61	62	63	64	65	66	67	68	69	70	71
Valency.	2	2	2		2	2				2			2	
	3	3	3	3	3	3	3	3	3	3	3	3	3	3
	4	4	4					4						

presents no analogy to the transition sub-period or to the main period, for these are real periods consisting of eight groups, whereas the elements of the transition sub-series do not exhibit valency less than two or greater than four, and thus cannot form a period. From time to time it has been proposed to place cerium in Group IV on the grounds of its quadrivalency and the isomorphism of some few of its salts with those of thorium and zirconium. These proposals have lost much of their point since the discovery of celtium (hafnium), properly allocated to Group IV because of its extraordinarily close resemblance to zirconium. It will, moreover, be shown, in discussing the electronic structure of atoms, that the allocation of cerium to Group III and to the transition sub-series on chemical grounds is fully justified, in that the electron responsible

for the increase in the valency of cerium from three to four is probably structurally unrelated to any of the electrons responsible for the quadrivalency of celtium (hafnium) or indeed of any element in either the main or transition periods.

The transition sub-periods (Table 3), based upon the foregoing considerations, comprise two typical periods each of ten elements, an abridged period also of ten elements, and a final incomplete period, all the periods commencing with Group III and ending with Group II.

With the possible exceptions of scandium and zinc (although scandium possesses an acetylenic carbide of the probable formula ScC_2, in which the metal would be bivalent), all the transition elements exhibit variable valency, and this variation can and usually does occur by one unit, instead of by the invariable two units of the abridged classification. With very few exceptions, the transition elements give rise to coloured salts, whereas the elements of the abridged classification form only colourless salts. Unlike the abridged periodic classification, the groups of which are divisible into a class of two alkaline groups, a second class of two amphoteric groups, and a third class of four non-basic groups, the transition classification consists of only one strongly basic group, III, the other seven groups almost without exception comprising only elements with either amphoteric or strongly acidic properties in their highest oxides, although the acidic properties are feeble in Groups I and II.

The Complete Periodic Classification.

On recombining the transition classification (Table 3) with the abridged classification (Table 2), the full periodic classification including the whole of the elements is obtained (Table 1). This table differs from the commonly accepted forms in small but important features. Seven main periods suffice to include all the known elements, a primitive period of two elements, two simple periods each of eight elements, and four complex periods consisting each of two sub-periods. Each period comprises only eight groups, commencing with Group I and ending with Group VIII, the simple periods and the main sub-periods of the long periods terminating with noble gases and the transition sub-periods with noble metals. In order to indicate their close resemblance to the noble metals of Group VIII, the pairs copper and zinc, silver and cadmium, and gold and mercury, are alternatively included also in this group, just as hydrogen is alternatively included in Group VII to indicate its resemblance to the halogen elements.

The transition elements in each long period are shown in heavy type, the arrows between elements of Groups II and III indicating

the position at which the transition elements create a gap between the typical elements of the periods. In order to preserve the symmetry of the octet classification, the 15 rare-earth elements, belonging to Group III and succeeding barium in atomic weight, are represented only by their most typical member, lanthanum, the other 14 being shown in detail in a footnote to the table. In order to facilitate the identification of the typical members of each group, which constitute the abridged classification, they are placed to the left and the transition elements to the right of the columns.

The abridged classification, the transition classification, the transition sub-series, and the complete periodic classification, shown in Tables 1, 2, 3, and 4, respectively, together with the experimental chemical evidence on which they are founded, will form the basis of subsequent papers on the interpretation of chemical evidence in terms of the distribution of electrons in atomic structures. The next paper will show primarily that the octet classification is due to the existence of from one to eight outer electrons in three sub-groups completed to 2, 2, 4 in the inert gases; that the transition classification is due to from one to eight more deeply seated electrons in two sub-groups completed to 4, 6 and forming part of a main group in five sub-groups of 2, 2, 4, 4, 6, completed in Group I; and that the transition sub-series is due to from one to fourteen still more deeply seated electrons completed to 6, 8, and forming part of a main group in seven sub-groups of 2, 2, 4, 4, 6, 6, 8, completed in lutecium. This scheme of atomic structure was first put forward by the author on incomplete evidence on March 9th, 1924 (*J. Soc. Chem. Ind.*, **43**, 323), and is now found to be fully justified in the light of additional evidence chiefly furnished by the foregoing periodic classifications.

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THE UNIVERSITY OF BIRMINGHAM,
EDGBASTON.

[*Received, May 25th*, 1927.]

CCLXVIII.—*Molecular Structure in Solution. Part II. The Refractive Indices and Surface Tensions of Aqueous Solutions of Cobalt Chloride and Hydrochloric Acid.*

By Owen Rhys Howell.

The densities and viscosities of a series of solutions having a fixed concentration of cobalt but increasing concentrations of hydrochloric acid, and also those of an exactly similar series of solutions of the acid alone, have already been determined (this vol., p. 158). It was shown that the differences in the densities of corresponding solutions varied with increasing concentration of acid, the curve exhibiting a point of inflexion. The differences in the viscosities of corresponding solutions also varied, the curve showing a well-defined maximum. The point of inflexion in the one case and the maximum in the other occurred at precisely the same concentration of acid.

The work of Hill and Howell (*Phil. Mag.*, 1924, **48**, 833) suggests that in the red pigments and solutions the cobaltous atom is surrounded by six other atoms or groups, whilst in the blue pigments and solutions it is surrounded by four, and the results outlined above were interpreted by assuming that with increasing concentration of acid, the cobalt atom is thrown out of its association with six molecules of water, $Co(H_2O)_6^{\cdot\cdot}$, into one with four atoms of chlorine, $CoCl_4''$. It was deemed of interest to determine other physical properties of these solutions in order to ascertain whether they also would show similar variations; the refractive indices and surface tensions have therefore been measured.

Experimental.

Determination of Refractive Index.—The measurements were made with a Pulfrich refractometer. In order that the results should be directly comparable with those already obtained for the densities and viscosities, all determinations were made at 20°.

Since all the solutions were acidic, it was impossible to utilise the usual attachment for temperature regulation. The whole instrument was therefore encased by means of asbestos mill-board cut to shape, and the temperature was kept constant to within $\pm 0{\cdot}5°$ by regulating a small gas flame placed inside the case. The cell was covered with a watch-glass to prevent loss of acid.

Measurements were made for the D line with a sodium flame, and for the C, F, and G′ lines with a hydrogen tube. The refractive index of every solution in the series containing acid only was deter-

the position at which the transition elements create a gap between the typical elements of the periods. In order to preserve the symmetry of the octet classification, the 15 rare-earth elements, belonging to Group III and succeeding barium in atomic weight, are represented only by their most typical member, lanthanum, the other 14 being shown in detail in a footnote to the table. In order to facilitate the identification of the typical members of each group, which constitute the abridged classification, they are placed to the left and the transition elements to the right of the columns.

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Measurements were made for the D line with a sodium flame, and for the C, F, and G′ lines with a hydrogen tube. The refractive index of every solution in the series containing acid only was deter-

mined for each of these lines, but this was impossible with the series containing cobalt since these solutions are coloured. Although the red solutions have strong absorption bands in the blue region, with the concentration of cobalt taken the F and G′ lines were transmitted sufficiently well to enable measurements to be made. The refractive index for each of these two lines has therefore been determined for every member of the series of solutions containing cobalt. The blue solutions, however, are much more intense than the red, and with these the C and D lines were completely extinguished. It was therefore possible to determine the refractive index for these two lines only with the solutions at the red end of the series.

Readings could be reproduced to within 1′ even with the faintest lines and to within 0·5′ with strong ones. The values of the refractive index are therefore all correct to the fourth place of decimals and most of them to within 5 units in the fifth place.

Determination of Surface Tension.—The measurements were made with a Traube stalagmometer. The lower capillary and also a long open tube were passed through a rubber stopper fitted into a small bottle. The stalagmometer was filled with the solution, and a little of this was also placed in the bottle in order to saturate with the vapour the atmosphere in which the drops formed. The apparatus was immersed vertically (against a plumb-line) in a glass-fronted thermostat kept at 20° ± 0·01°. The surface tension was calculated from the formula

$$\gamma_{\text{sol.}} = \gamma_{\text{water}} \times n_w/n_s \times d_s,$$

where n_w and n_s are the number of drops given by water and by the solution respectively, and d_s is the relative density of the solution. The value $\gamma_{20°} = 72{\cdot}69$ for water was employed, and the values of the relative density used were those determined in the previous investigation.

It has been shown (Lohnstein, *Z. physikal. Chem.*, 1908, **64**, 686; 1913, **84**, 410; Harkins and Humphery, *J. Amer. Chem. Soc.*, 1916, **38**, 228; Harkins and Brown, *ibid.*, 1919, **41**, 499) that the simple formula for the surface tension requires a correction factor depending on the ratio of the radius of the tip to the linear dimensions of the drop. If r is the radius of the tip and v the volume of the drop, then when $r/v^{\frac{1}{3}}$ lies between 0·76 and 0·95 the correction is practically constant. In a comparative method of determining surface tension the correction factor would then cancel, leaving the equation given above as a true expression.

The diameter of the tip of the stalagmometer used for these experiments was 0·87 cm. The volumes of the largest drops (given

by water) and of the smallest (given by the most concentrated acid solution) were determined by weighing and found to be 0·1268 c.c. and 0·1021 c.c., respectively. The extreme values of the ratio r/v are therefore 0·865 and 0·930. Since these fall within the limits for the constancy of the correction factor, the simple equation used for the calculation is sufficiently accurate.

With the solution yielding the smallest drops, each drop corresponded to 18 divisions on the scale. Since the determinations could be reproduced to within 0·5—1·0 division, the measurements are correct to within about $\pm$ 3 units in the second place of decimals. At least two determinations were made for each solution and the mean was taken.

The tip of the stalagmometer was freed from grease by being dipped in chromic acid solution before each determination and the whole apparatus was similarly cleansed at intervals. The drop number for water was checked from time to time and found to remain quite constant at 55·55 drops.

Materials.—As in the previous investigation, the hydrochloric acid employed was the pure commercial product and the cobalt chloride was Kahlbaum's purest, free from iron and nickel. All the water used was the laboratory distilled water, redistilled with precautions to preclude contamination by dust or grease.

Solutions.—Three stock solutions were prepared: cobalt chloride in water (120 g. of $CoCl_2,6H_2O$ per litre), cobalt chloride in concentrated hydrochloric acid (120 g. of $CoCl_2,6H_2O$ per litre), and hydrochloric acid in water. Their concentrations were adjusted to exactly the same values as those employed in the previous investigation. All the other solutions were prepared from these by dilution in the manner already described (*loc. cit.*).

Note on the Density of Aqueous Hydrochloric Acid.—It was not stated in the previous paper that in preparing the stock solution of hydrochloric acid by diluting the fuming acid, the solutions were cooled in iced water to minimise loss of acid. The stock solution was therefore 10·63*N* at 0° = 32·88% of HCl (by weight). In the present investigation, a solution of the acid having exactly the same density was found by titration against pure sodium carbonate to be 10·48*N* at 18°. The solution therefore contained 32·80% of HCl, a figure in good agreement with that previously found. The densities of the series of solutions prepared by diluting the stock solution were checked and found to agree with those obtained previously to within 1 unit in the fourth place of decimals.

In order to complete the series of values up to the fuming acid, the densities and viscosities of three more concentrated solutions have been determined; these are shown in Table I together with

the true normality of the solution at 18° and the composition by volume and by weight. The concentrations are correct to 0·2%, the densities to within 2 units in the fourth place of decimals and the viscosities to within 0·1%.

TABLE I.

Densities and Viscosities of Aqueous Solutions of Hydrochloric Acid.

Concentration of HCl.					
Normality, $N_{18°}$.	% by vol.	% by weight.	Relative density, $d^{20°}_{20°}$.	Absolute density, $d^{20°}_{4°}$.	Viscosity, $\eta_{20°}$.
0	0	0	1·0000	0·9982	0·01005
1·048	3·821	3·757	1·0186	1·0168	0·01065
2·096	7·642	7·385	1·0364	1·0346	0·01125
3·144	11·46	10·89	1·0536	1·0518	0·01187
4·192	15·28	14·29	1·0707	1·0689	0·01251
5·240	19·11	17·59	1·0871	1·0852	0·01323
6·288	22·93	20·80	1·1036	1·1016	0·01408
6·498	23·69	21·43	1·1067	1·1048	0·01430
6·812	24·84	22·37	1·1112	1·1092	0·01452
7·126	25·98	23·30	1·1162	1·1142	0·01482
7·336	26·75	23·91	1·1195	1·1176	0·01500
7·860	28·66	25·43	1·1275	1·1255	0·01555
8·384	30·57	26·94	1·1355	1·1335	0·01611
9·432	34·39	29·90	1·1507	1·1487	0·01731
10·48	38·21	32·80	1·1657	1·1637	0·01870
11·48	41·86	35·53	1·1789	1·1768	0·02004
12·83	46·78	39·14	1·1957	1·1935	0·02183
13·38	48·78	40·61	1·2020	1·1998	0·02266

The curve obtained on plotting the densities against the % of HCl by weight is almost a straight line up to 33%, being only very slightly concave to the axis of concentration. The last three values, however, fall below the extended curve, which is in agreement with the values recorded by other observers (Landolt and Bornstein's Tables, 1923, p. 394).

Results.

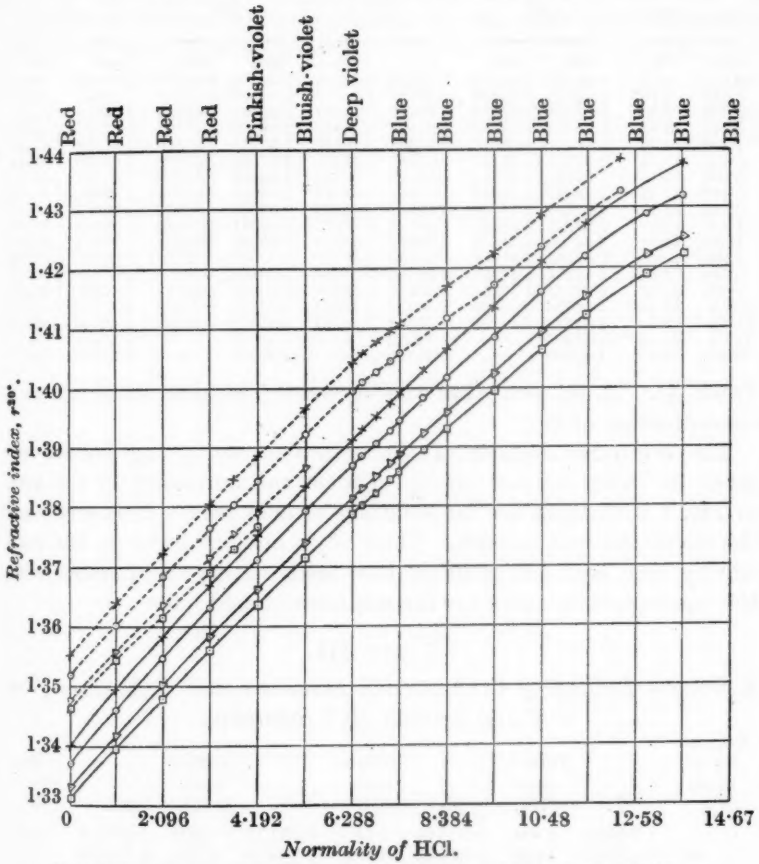
Refractive Indices.—The values of the refractive indices of the solutions of hydrochloric acid only, measured as already described, are given in Table II, and plotted against the normality of the solution in Fig. 1. It is seen that almost throughout their entire length all four curves exhibit a gradual increase of concavity to the axis of concentration. They fall more rapidly near the end, the values for the two highest concentrations of acid being lower than those anticipated from the general course of the curves. Each of the curves is expressed with very fair accuracy by an equation of the form

$$r_{sol.} = r_{water} + xN - yN^2,$$

where N is the normality of the solution and x and y are constants.

FIG. 1.

Colour of the cobalt solution in transmitted light.



Dotted line curves : Solutions of hydrochloric acid + cobalt chloride.
Full-line curves : Solutions of hydrochloric acid only.

Refractive index for the G′ *line shown thus :* ×.
" " " F " " " ⊙.
" " " D " " " △.
" " " C " " " ⊡.

The values calculated from the equations

$$r_{C}^{20°} = 1{\cdot}33117 + 0{\cdot}008090N_{18°} - 0{\cdot}0000862N_{18°}^{2}$$
$$r_{D}^{20°} = 1{\cdot}33299 + 0{\cdot}008330N_{18°} - 0{\cdot}0001000N_{18°}^{2}$$
$$r_{F}^{20°} = 1{\cdot}33703 + 0{\cdot}008630N_{18°} - 0{\cdot}0001083N_{18°}^{2}$$
$$r_{G'}^{20°} = 1{\cdot}34017 + 0{\cdot}008850N_{18°} - 0{\cdot}0001129N_{18°}^{2}$$

are given in italics in the columns next to the observed values in

Table II.

Refractive Indices of Aqueous Solutions of Hydrochloric Acid.

Conc. of HCl,		$r_C^{20°}$.		$r_D^{20°}$.		$r_F^{20°}$.		$r_{G'}^{20°}$.	
$N_{18°}$.	%.	obs.	calc.	obs.	calc.	obs.	calc.	obs.	calc.
0	0	1·33117	*1·33117*	1·33299	*1·33299*	1·33703	*1·33703*	1·34017	*1·34017*
1·048	3·757	1·33938	*1·33956*	1·34173	*1·34161*	1·34599	*1·34595*	1·34944	*1·34933*
2·096	7·385	1·34786	*1·34775*	1·35007	*1·35001*	1·35464	*1·35464*	1·35824	*1·35823*
3·144	10·89	1·35594	*1·35575*	1·35815	*1·35819*	1·36305	*1·36309*	1·36684	*1·36687*
4·192	14·29	1·36357	*1·36357*	1·36603	*1·36615*	1·37111	*1·37130*	1·37521	*1·37529*
5·240	17·59	1·37135	*1·37120*	1·37387	*1·37389*	1·37922	*1·37927*	1·38339	*1·38344*
6·288	20·79	1·37863	*1·37863*	1·38127	*1·38142*	1·38686	*1·38701*	1·39121	*1·39136*
6·498	21·43	1·38027	*1·38010*	1·38304	*1·38291*	1·38850	*1·38853*	1·39302	*1·39291*
6·812	22·37	1·38230	*1·38228*	1·38503	*1·38509*	1·39059	*1·39079*	1·39517	*1·39522*
7·126	23·30	1·38442	*1·38444*	1·38713	*1·38727*	1·39281	*1·39303*	1·39745	*1·39751*
7·336	23·91	1·38592	*1·38589*	1·38867	*1·38872*	1·39449	*1·39451*	1·39903	*1·39901*
7·860	25·43	1·38962	*1·38945*	1·39238	*1·39229*	1·39830	*1·39817*	1·40305	*1·40276*
8·384	26·94	1·39294	*1·39295*	1·39572	*1·39580*	1·40169	*1·40176*	1·40646	*1·40643*
9·432	29·90	1·39945	*1·39981*	1·40218	*1·40266*	1·40851	*1·40879*	1·41350	*1·41360*
10·48	32·80	1·40654	*1·40649*	1·40950	*1·40931*	1·41600	*1·41557*	1·42111	*1·42052*
11·48	35·53	1·41224	*1·41269*	1·41542	*1·41544*	1·42209	*1·42183*	1·42743	*1·42688*
12·83	39·14	1·41907	—	1·42232	—	1·42915	—	1·43454	—
13·38	40·61	1·42203	—	1·42522	—	1·43222	—	1·43784	—

Table II. It is seen that the agreement is quite good up to a concentration of 10*N*.

The refractive indices of the solutions containing cobalt are given in Table III and plotted against the normality of the acid in Fig. 1 with those for the solutions of acid only. It is seen that the curves are not smooth. There is an obvious break in the continuity, and each curve ultimately tends to become parallel with the corresponding curve for the solutions of acid only.

Table III.

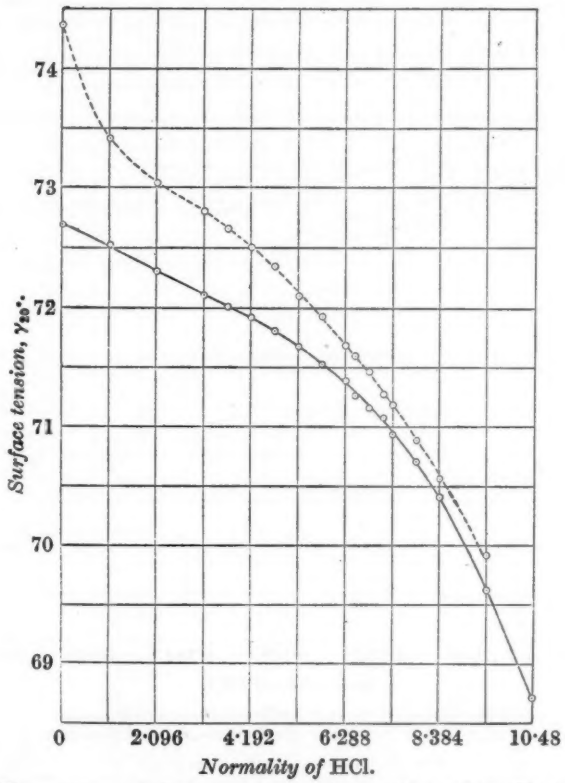
Refractive Indices of $CoCl_2$ + HCl *Solutions and Differences from Corresponding* HCl *Solutions.*

Normality of acid, $N_{18°}$.	$r_C^{20°}$.	Difference $\times 10^5$.	$r_D^{20°}$.	Difference $\times 10^5$.	$r_F^{20°}$.	Difference $\times 10^5$.	$r_{G'}^{20°}$.	Difference $\times 10^5$.
0	1·34621	1504	1·34744	1445	1·35172	1469	1·35524	1507
1·048	1·35437	1499	1·35564	1391	1·36019	1420	1·36390	1446
2·096	1·36147	1361	1·36367	1360	1·36844	1380	1·37236	1412
3·144	1·36899	1305	1·37142	1327	1·37646	1341	1·38056	1372
3·668	1·37283	1308	1·37541	1332	1·38039	1331	1·38463	1361
4·192	1·37655	1298	1·37906	1303	1·38435	1324	1·38864	1343
4·716			1·38294	1299	1·38828	1312	1·39270	1340
5·240			1·38670	1283	1·39225	1303	1·39673	1334
6·288					1·39957	1271	1·40415	1294
6·498					1·40093	1243	1·40568	1266
6·812					1·40269	1210	1·40767	1250
7·126					1·40449	1168	1·40932	1187
7·336					1·40583	1134	1·41065	1162
8·384					1·41169	1000	1·41693	1047
9·432					1·41726	875	1·42268	918
10·48					1·42366	766	1·42913	802
12·26					1·43301	641	1·43853	673

If the cobalt atom were similarly associated in all these solutions, the refractive index should change regularly with increasing con-

centration of acid, as it does with the solutions of acid alone. Since this is not so, it follows that the cobalt atom undergoes a change in its association as the concentration of acid is increased; a suggestion as to the nature of this change has been given on p. 2039 and its course may be followed by considering the differences of the refractive indices of corresponding solutions. The values

FIG. 2.



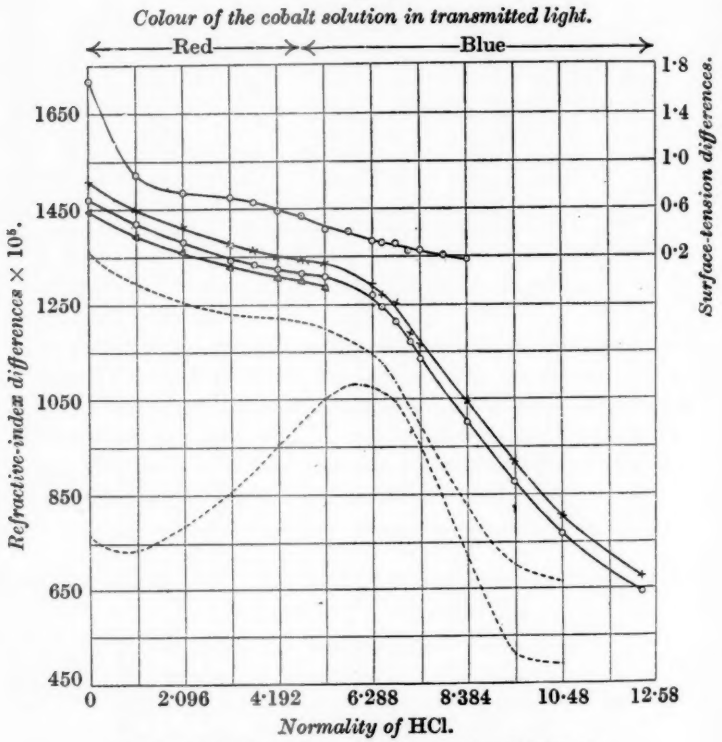
Upper curve: Solutions of hydrochloric acid + cobalt chloride.
Lower curve: Solutions of hydrochloric acid only.

obtained on subtracting the refractive indices of the solutions of hydrochloric acid alone from those of the corresponding solutions containing cobalt are given in Table III and plotted against the normality of the acid in Fig. 3.

The resulting curves are precisely similar to the curve obtained in the previous investigation by plotting the density differences against the concentration of acid. They exhibit well-marked inflexions at the same concentration of acid as the inflexion of the

density-differences curve and as the maximum of the viscosity-differences curve (both of which are reproduced in Fig. 3 for comparison). It is seen that towards the end of its course each curve is flattening out (although not as sharply as the density-differences curve) to become parallel to the axis of concentration, thus indicat-

FIG. 3.



Upper full-line curve : Surface-tension differences.
Lower full-line curves : Refractive-index differences.

For the G′ line, shown thus : ×.
" " F " " " ⊙.
" " D " " " △.

Upper dotted-line curve : Density differences.
Lower dotted-line curve : Viscosity differences.

ing that the change to the $CoCl_4''$ configuration is nearing completion, where further increase in the concentration of acid could no longer affect the state of the cobalt atom.

The refractive index of the blue form is evidently less than that of the red. As the concentration of acid is increased and the change from red to blue proceeds, the curve falls continuously but not regularly. The diminution of the difference of refractive index,

like that of the density difference, takes place at first very gradually and then very rapidly. The suggestion offered to account for this feature in the density-differences curve also explains the same form of the refractive index-differences curve. The $Co(H_2O)_6^{\cdot\cdot}$ ions are progressively converted into $CoCl_4''$ ions, and as these are oppositely charged there is a powerful attraction between them. Evidently this attraction will be a maximum when equal numbers are present in the solution, and it is suggested that this condition obtains at the point of inflexion.

Surface Tensions.—The values of the surface tensions for the two series of solutions are given in Table IV and plotted in Fig. 2. Previous determinations of the surface tension of some aqueous solutions of hydrochloric acid alone have been made by Volkmann (see Landolt and Bornstein's Tables, 1923, p. 238) using the capillary-rise method. The values are in fair agreement with those now reported, which lie on a smooth curve. An equation has not been found to express the whole curve, but if the logarithm of the

TABLE IV.

Surface Tensions.

1.	2.	3.	4.	5.	6.
		Surface tension of			
Conc. of HCl,		$CoCl_2$+HCl.	HCl alone.		Difference,
$N_{18°}$.	%.	$\gamma_{20°}$.	$\gamma_{20°}$ (obs.).	$\gamma_{20°}$ (calc.).	(3—5).
0	0	74·36	72·69	—	1·67
1·048	3·757	73·41	72·52	—	0·89
2·096	7·385	73·04	72·30	—	0·74
3·144	10·89	72·80	72·10	*72·10*	0·70
3·668	12·63	72·66	72·00*	*72·01*	0·65
4·192	14·29	72·50	71·91	*71·92*	0·58
4·716	15·97	72·34	71·80*	*71·80*	0·54
5·240	17·59	72·09	71·67	*71·67*	0·42
5·764	19·20	71·92	71·52	*71·52*	0·40
6·288	20·79	71·68	71·38	*71·36*	0·32
6·498	21·43	71·59	71·26	*71·28*	0·31
6·812	22·37	71·46	71·15	*71·16*	0·30
7·126	23·30	71·27	71·07	*71·03*	0·24
7·336	23·91	71·18	70·92	*70·94*	0·24
7·860	25·43	70·88	70·70	*70·68*	0·20
8·384	26·94	70·56	70·40	*70·39*	0·17
9·432	29·90	69·91	69·62	*69·66*	0·25
10·48	32·80	—	68·71	*68·71*	—

(Column 2 refers only to the solutions of hydrochloric acid alone.)

* These two values are read from the curve shown in Fig. 2.

difference, Δ, between the surface tension of water and that of each solution be plotted against the concentration of the solution, all the points except the first three lie on a perfectly straight line. The equation to the line is

$$\log \Delta = 0{\cdot}1130N_{18°} - 0{\cdot}5850$$

where $\Delta = \gamma_{water} - \gamma_{sol.}$, and $N_{18°}$ is the normality of the solution at 18°. The values of the surface tension calculated from this expression are given in column 5 of Table IV. Comparing them with the observed values in column 4, it is seen that the agreement is within the limits of experimental error.

It was found impossible to get very concordant values of the drop number with the more concentrated acid solutions. They indicate, however, that the surface tensions of these solutions are progressively higher than those anticipated from the general course of the curve. It will be recalled that the densities of these solutions were lower than demanded by the form of the density curve.

The curve for the solutions containing cobalt, on the other hand, obviously consists of two parts, the first (for lower concentrations of acid) being convex to the axis of concentration, and the second (for higher concentrations of acid) being concave to this axis, and eventually becoming parallel to the curve for the solutions of acid alone.

The change in the association of the cobalt atom may again be followed by examining the differences of the surface tensions of the solutions containing cobalt and the corresponding solutions containing acid only. These differences are given in column 6 of Table IV and are plotted against the normality of acid in Fig. 3. It is seen that the curve is again of the same type as the density-differences curve and the refractive index-differences curves, but it differs from these in two important particulars.

The first of these is that the curve falls away rapidly from the initial value, whereas both the density-differences and the refractive index-differences curves fall off gently from the beginning. This characteristic of the surface tension-differences curve is readily explained. It is seen from the values of the surface tensions in Table IV and from the curves in Fig. 2 that the first solution in the series containing cobalt (*i.e.*, aqueous cobalt chloride alone) has a surface tension greater than that of water; so also have the solutions immediately following. That is, the cobalt atom in its red association, $Co(H_2O)_6^{\cdot\cdot}$, *raises* the surface tension of water. It follows from the Gibbs equation that the concentration of this ion in the surface layer is *less* than that in the bulk of the solution.

It is evident from the curves in Fig. 2 that the blue solutions (those having a high concentration of acid) have a surface tension only slightly higher than the corresponding solutions containing acid alone. Assuming that the whole of the acid is " free " in these cobalt solutions, as in the solutions of acid alone, it follows that the cobalt atom in its blue association, $CoCl_4''$, also raises the surface tension of water, but to a far smaller extent than does the

red $Co(H_2O)_6^{\cdot\cdot}$. It is quite probable, however, since the acid is not wholly free but partly bound in the form of these complex ions, that the surface tension of the blue solutions is actually less than that of solutions of acid alone having a concentration equal to that of the "free" acid. In this event, the blue form, $CoCl_4''$, *lowers* the surface tension of water, and in accordance with the Gibbs equation its concentration in the surface layer is *greater* than in the bulk.

Even if the blue form raises the surface tension, it follows that for a given bulk concentration of cobalt, its concentration in the surface layer would be greater than that of the red form. When, therefore, the first introduction of acid to the cobalt solution results in the conversion of some $Co(H_2O)_6^{\cdot\cdot}$ ions into $CoCl_4''$ ions, the same change takes place in the surface layer to a far greater degree. The increase in concentration of the blue form is therefore far greater in the surface layer than in the bulk of the solution. The surface tension, which is a purely surface phenomenon, is a measure of this change, so that the surface tension-differences curve falls rapidly with the initial increases in acid concentration, whereas the density-differences curve and the refractive index-differences curves, indicating the effect in the bulk of the solution, fall away gradually.

The second particular in which the surface tension-differences curve differs from the others is that it exhibits its inflexion at a different concentration of acid. This also is to be expected and is explicable on the same reasoning. It has been suggested that the point of inflexion in the density-differences curve and in the refractive index-differences curves and also the maximum in the viscosity-differences curve occur when the solution contains equal amounts of the two kinds of ions, $Co(H_2O)_6^{\cdot\cdot}$ and $CoCl_4''$, since the attraction between them will then be greatest. It is now suggested that the point of inflexion in the surface tension-differences curve corresponds to the concentration of acid at which the same conditions obtain in the surface layer. Since the blue form accumulates in the surface layer to the exclusion of the red form, it follows that there will be equal amounts of each in the surface layer before this state is reached in the bulk of the solution. The surface tension-differences curve should therefore exhibit inflexion before the corresponding curves for the other properties which are dependent on the conditions in the bulk. It is seen from Fig. 3 that this is so.

It should be noted that although replacement of half the red form by the blue occurs in the surface layer sooner than in the bulk, the complete replacement cannot occur until this change is also

complete in the bulk. So long as any of the red form remains in the solution, a corresponding amount will be present in the surface layer, and it is not until all the red form has been converted in the solution that the same state is reached in the surface layer. The surface tension-differences curve should therefore not flatten out and become parallel to the axis of concentration sooner than the other curves, but at the same concentration of acid. It is seen from Fig. 3 that the curve falls continuously from the point of inflexion and has not become parallel over the range examined, but there are indications that this condition will be reached as with the other curves.

The Colour Change.—In the previous investigation, the colours of the cobalt solutions recorded were those observed by viewing thin layers against a white ground. In the present paper the colours of layers 5 cm. thick viewed in transmitted daylight are given at the head of Fig. 1.

The solutions having an acid concentration up to 3·144*N* are definitely red when examined in either thin or thick layers. Those having a concentration greater than 6·288*N* are green in very thin layers, but definitely blue with no trace of green in thicker layers. This dichroism is very marked.

Whereas these definitely red and blue solutions are clear and " clean," those lying within the limits stated are dull and " muddy " in appearance. In thin layers, the colour is indefinite. Thus the 4·192*N*-solution was previously described as brownish-red; in a thick layer, however, it is pinkish-violet, being definitely reddish with a tinge of blue. The 5·240*N*-solution, which is the most indefinite, was called a dull brown, but would have been better described as a dull amethyst, for even in thin layers it has a distinct blue tinge. In thicker layers the solution is definitely blue with a faint tinge of red. The 6·288*N*-solution is a very deep violet. The change in colour is therefore gradual and extends over a fair range of acid concentration. The 4·192*N*-solution being more red than blue, and the 5·240*N*-solution being more blue than red, the maximum colour change occurs between these concentrations of acid, as indicated at the head of Fig. 3. The 4·716*N*-solution, mid-way in acid concentration between these two, appears to be very nearly half red and half blue.

It was pointed out in the previous investigation that the point of inflexion in the density-differences curve and the maximum in the viscosity-differences curve do not coincide with the maximum change in colour, but at a considerably higher concentration of acid. The same is now seen to be true for the refractive index-differences curve. The colour change therefore takes place before

even half the cobalt has been transformed from the red to the blue association and this is in accordance with the fact already pointed out, that the blue form is far more intense than the red.

It should be noted that the concentration of acid at which the two forms are in equal amount in the surface layer, as indicated by the surface tension-differences curve, also does not correspond to the concentration at which the change of colour occurs.

Summary.

1. The refractive indices and surface tensions of a series of aqueous solutions containing a constant amount of cobalt chloride and increasing amounts of hydrochloric acid have been determined.

2. The same constants of an exactly similar series containing hydrochloric acid alone have also been measured.

3. The differences in the values for corresponding solutions bring to light the effect of the acid on the cobalt in solution.

4. The curve showing the differences in refractive index plotted against the concentration of acid is exactly similar to that of the density differences found in a previous investigation. The point of inflexion in both occurs at the same concentration of acid and is accounted for on the same reasoning.

5. The curve showing the differences in surface tension is also similar, but has a sharp initial fall and exhibits its point of inflexion at a lower concentration of acid. These two differences are wholly explained by the facts (*a*) that the surface tension is a measure of the conditions prevailing in the surface layer while the other properties are a measure of those in the bulk of the solution, and (*b*) that the relative concentrations of the red and the blue cobalt ions in the surface layer are different from those in the bulk under any given conditions.

6. The change in colour of the cobalt solutions with increasing acid concentration is discussed.

The author would express his sincere thanks to Prof. F. L. Pyman, F.R.S., for giving him every facility for prosecuting this work.

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CCLXIX.—*Formation and Decomposition of Ketone Cyanohydrins, with Special Reference to some Compounds recently classified as such.*

By ARTHUR LAPWORTH, RICHARD HELMUTH FRED MANSKE, and EDWIN BREW ROBINSON.

IN a recent paper (*Ber.*, 1927, **60**, 586) Houben and Pfankuch described some new nitriles two of which were considered to be the stereoisomeric cyanohydrins of camphor. These workers commented on the remarkable stability of these nitriles, which did not show any tendency to dissociate into hydrogen cyanide and ketone; but having also found that the direct union of hydrogen cyanide and camphor cannot be effected, they concluded that these observations illustrate the rule that "ein Korper, der schwer entsteht, meistens schwer wieder zerfällt" (*loc. cit.*, p. 587).

Houben and Pfankuch described another new nitrile which they regarded as "menthon-cyanohydrin" (*loc. cit.*, p. 599). They did not state specifically that this compound has the same remarkable stability as the supposed camphor cyanohydrins, but, as they were able to purify it (apparently without adopting any special precautions) from boiling ligroin and to hydrolyse it with methyl-alcoholic potassium hydroxide, there can be no doubt that the compound was much more stable than most of the known cyanohydrins of other simple ketones.

Passerini, in a still more recent paper (*Ber.*, 1927, **60**, 1201, 1202), accepts the views of Houben and Pfankuch, but finds that the supposed "menthon-cyanohydrin" described by these authors is converted on hydrolysis with acids into a lactone, and infers that here "das Hydroxyl des Menthon-cyanohydrin in den Menthan-Ring wandert." Such a migration in a saturated compound has no parallel within the knowledge of the present authors.

A long series of measurements of equilibria in systems containing cyanohydrin, hydrogen cyanide and ketone (or aldehyde) in aqueous alcohol has been made in these laboratories during the last 3 years and among the cases studied were those comprising camphor and menthone respectively. It was found that, out of some 60 ketones and aromatic aldehydes examined, only 2, benzophenone and camphor, gave no detectable amounts of cyanohydrin by direct combination with hydrogen cyanide. With the others, a sensibly constant equilibrium condition was attained within 24 to 36 hours at most in aqueous alcohol, if a very small proportion of tripropylamine was present as catalyst. The dissociation constants of the cyanohydrins varied very widely, ratios of extremes observed being

at least 1 : 25,000, and the failure of camphor and benzophenone to yield measurable quantities of cyanohydrin is doubtless to be ascribed to the exceptionally high dissociation constants of the cyanohydrins rather than to catastrophic disappearance of reaction velocity.

It is quite otherwise in the case of menthone, the cyanohydrin * of which is formed quite readily in the cold, the time required in the above conditions to attain a concentration practically identical with the equilibrium value not exceeding 24 hours.

Experiment A illustrates some of these statements: Menthone (11·38 g.), 2 c.c. of ethyl alcohol containing 0·24 g. of tripropylamine, and 5 c.c. of anhydrous hydrogen cyanide dissolved in cold dry methyl alcohol (about 30 c.c.) were mixed and left over-night in a stoppered flask, previous experience having shown that further contraction (initially attendant on combination) is inappreciable after such a period. The vessel was then opened, the contents made up to 50 c.c. with more dried methyl alcohol, and the flask again closed with a waxed stopper and allowed to remain in an ice-chest for 60 hours, a period considerably exceeding that (24—36 hours) which previous experiments, under not wholly dissimilar conditions, had shown to be amply sufficient for the attainment of a practically steady state.† The solution was then analysed by a method based on that of Ultée (*Rec. trav. chim.*, 1909, **28**, 248), which depends on the fact that in presence of mineral acid, silver nitrate in the cold precipitates only cyanidion which is not in combination with the aldehyde or ketone. An aliquot portion of the solution was removed and at once added to excess of standard silver nitrate solution acidified with nitric acid, the whole being shaken, and the silver cyanide removed by filtration. The excess of silver in the filtrate was determined by titration with standard thiocyanate in the usual way. The free hydrogen cyanide present in the original 50 c.c. of solution was thus found to be 1·95 g.

Another portion of the solution was removed and allowed to remain in the cold with five times its bulk of *N*-sodium hydroxide for 45 minutes. The whole was acidified with nitric acid and mixed with excess of standard silver nitrate and the excess of silver was determined as before. The total hydrogen cyanide found in this way was 3·49 g. (comparing favourably with 3·53 g. found in the

* Strictly speaking, as menthone itself is a mixture of two dynamic isomerides, each of which can theoretically give rise to two stereoisomeric addition compounds with hydrogen cyanide, the cyanohydrin formed as above must be a mixture of four isomerides.

† A blank experiment in which the menthone was omitted showed that the total amount of hydrogen cyanide remaining after these manipulations would be approximately 3·53 g. if no combination had taken place.

blank experiment above mentioned). It is probable that a minute but hardly measurable quantity of the sodium derivative of the cyanohydrin remains in equilibrium with menthone and cyanidion in presence of sodium hydroxide:

$$C_{10}H_{18}O + CN' \rightleftharpoons C_{10}H_{18}(CN)\cdot O'.$$

From the titres, it may be deduced (1) that at equilibrium under the conditions specified above, 1 mol. of menthone is converted to the extent of about 0·8 mol. into cyanohydrin, in equilibrium with which 0·2 mol. of unchanged menthone remains with about 1 mol. of uncombined hydrogen cyanide, (2) that menthone cyanohydrin is almost completely converted into menthone and sodium cyanide by cold *N*-sodium hydroxide in not more than 45 minutes, the rapid acidification preventing appreciable recombination.

While the equilibrium may be effectively "frozen" by excess of mineral acid in aqueous or dilute alcoholic solution (as is shown by the failure of silver nitrate to decompose the cyanohydrin in these circumstances), it has not been found possible to separate the cyanohydrin from unchanged menthone owing to the instability of the former. It is quite easy to convert menthone to the extent of 90% into mixed cyanohydrins with excess of anhydrous hydrogen cyanide in presence of a trace of tripropylamine; but when attempts were made to remove hydrogen cyanide at the ordinary temperature by the use of a vacuum, even after adding some excess of hydrogen chloride in ether in the endeavour to stabilise the cyanohydrin, the latter underwent considerable decomposition and in the end constituted only about 30% of the residual oil.

On subjecting the equilibrium mixtures to hydrolytic action of mineral acids, including sulphuric acid, concentrated or dilute, in the cold, no evidence was obtained of the formation of any acid amide or carboxylic acid, and Pinner's method for the conversion of nitriles into imino-ethers in ethereal solution also gave negative results; the nitrile group is, in fact, extremely resistant to cold acid hydrolysts. If the temperature be raised, thermal dissociation occurs and hydrogen cyanide is lost, again before any effective hydrolysis has taken place. With alkalis, as has been demonstrated, the cyanohydrin is almost quantitatively decomposed even in the cold in a short time—probably within a few seconds. The great speed at which equilibrium is reached from either side in systems comprising ketone and cyanohydrin in presence of considerable concentrations of hydroxylion or cyanidion or both is perhaps not generally realised. *Experiment B* is described to illustrate the last point.

B. Cold saturated aqueous potassium cyanide (1 c.c.) at about

20° is shaken in a test-tube with 0·2 c.c. of *cyclo*hexanone which has been purified through the bisulphite compound. The ketone, at first immiscible, very quickly disappears, if the temperature is initially about 15°, a clear solution being formed with rise of temperature; then, as a rule, crystals of the potassium derivative of the cyanohydrin almost at once begin to appear and the whole sets, within about 30 seconds from the beginning of the experiment, to a semi-solid mass.

How little the concentration of *free* hydrogen cyanide affects the addition process may also be observed by repeating the experiment with the previous addition of 0·5 c.c. of 30% aqueous potassium hydroxide to the potassium cyanide. Although the concentration of free hydrogen cyanide due to salt hydrolysis must be reduced thereby many thousand-fold, the same phenomena are observed, while the time taken for setting is not more than doubled. The apparent decrease in speed is doubtless due in the main to the salting-out action of the potassium hydroxide reducing the already small solubility of the *cyclo*hexanone in the aqueous phase.

Observations already mentioned show that menthone cyanohydrin is readily formed and decomposed even in the cold in alkaline media and therefore, if the phenomena just described are not reproduced when menthone is used instead of *cyclo*hexanone, it is not because reaction is indefinitely delayed, but because the dissociation constants of menthone cyanohydrin and of its potassium derivative are much higher than those of *cyclo*hexanone cyanohydrin and of its potassium derivative respectively.* If, therefore, the compound described by Houben and Pfankuch were, in fact, menthone cyanohydrin, then at a very early stage in the alkaline hydrolysis which they carried out (*loc. cit.*, p. 600) equilibrium must have been attained, and this equilibrium should be reached no less rapidly by simply boiling menthone with potassium cyanide and potassium hydroxide in methyl-alcoholic solution, and with similar results on allowing hydrolysis to proceed. *Experiment C* was therefore carried out.

C. Menthone (10 g.) with potassium cyanide (10 g., or 2·5 mols.) and methyl alcohol (100 c.c.) was heated on the steam-bath for 48 hours. (A small portion of the product was removed at this point and worked up for carboxylic acid, but none could be detected.) Potassium hydroxide (25 g.) was next added and the heating was continued for a further 70 hours. On working up the whole for carboxylic acid, 1·9 g. of oily product, sparingly soluble in water but

* The dissociation constants of the two cyanohydrins in aqueous alcoholic solution at the ordinary temperature have been measured by one of us (R. H. F. M.) and found to be roughly in the ratio 72 : 1.

readily soluble in aqueous sodium carbonate, were isolated. Doubtless Houben and Pfankuch would have commented on such a poor yield after so prolonged a period of heating, but they do not mention either. It may be added that on attempting to convert the acid material into amide by the method used by Houben and Pfankuch only a small proportion of the product was soluble in hot ligroin, and even that portion failed to yield any crystalline solid.

Conclusions.—True menthone cyanohydrin, *i.e.*, the mixture of cyanohydrins produced by addition of hydrogen cyanide to ordinary menthone, is readily formed and decomposed reversibly in solutions which are at all alkaline and its properties indicate that Houben and Pfankuch were dealing with quite another compound. The characters ascribed by these workers to the compounds which they describe as camphor cyanohydrins are also at variance with those of all known ketone cyanohydrins.

It is suggested that a transformation of the Wagner type occurs when the nitrogen atom is separated from carbon in the experiments described by Houben and Pfankuch.

THE UNIVERSITY, MANCHESTER. [*Received, July 5th*, 1927.]

CCLXX.—l-*Methylephedrine, an Alkaloid from* Ephedra *Species.*

By SYDNEY SMITH.

THE Chinese drug Ma Huang derived from an *Ephedra* species has become of importance in Western medicine as the source of *l*-ephedrine, an alkaloid which has recently been found to possess a physiological action resembling that of adrenaline. In addition to *l*-ephedrine the drug contains *d*-*ψ*-ephedrine, and another alkaloid, the subject of the present communication, has now been isolated.

The constitutions of *l*-ephedrine and *d*-*ψ*-ephedrine

(OH·CHPh·CHMe·NHMe)

have been established beyond doubt by syntheses of the racemic bases and their resolution into the corresponding enantiomorphic forms, two of which are identical with the naturally occurring alkaloids *l*-ephedrine and *d*-*ψ*-ephedrine. The empirical formula and properties of the new alkaloid suggested that it was probably the *N*-methyl derivative of either *l*-ephedrine or *d*-*ψ*-ephedrine. The *N*-methyl derivatives were therefore prepared by methylation of the natural bases and it was found that the m. p. and specific rotation of *l*-methylephedrine were identical with those of the new alkaloid. Comparison of the m. p. and specific rotation of the

corresponding hydrochlorides and the methiodides afforded ample confirmation that the new alkaloid is identical with *l*-methylephedrine, $OH{\cdot}CHPh{\cdot}CHMe{\cdot}NMe_2$.

EXPERIMENTAL.

The syrupy alkaloidal residue obtained in the manufacture of ephedrine, freed as completely as possible from *l*-ephedrine and *d*-ψ-ephedrine, was purified by distillation under reduced pressure and neutralised with aqueous oxalic acid and the solution was evaporated to dryness. The residue on extraction with alcohol gave an alcohol-soluble fraction, which was dissolved in water and treated with a saturated aqueous solution of picric acid. The oil which first separated became solid on standing, and subsequent crops separated in a crystalline condition. The picrate was treated with hydrochloric acid and ether, and the resulting solution of the hydrochloride evaporated to dryness. The residue, after several crystallisations from alcohol, gave l-*methylephedrine hydrochloride* in stout, colourless tablets, m. p. 188—189° (corr.) (Found: C, 61·3; H, 8·3; Cl, 16·2. $C_{11}H_{17}ON,HCl$ requires C, 61·2; H, 8·4; Cl, 16·4%). It is readily soluble in water, less soluble in alcohol, and sparingly soluble in acetone. In water solution, it had $[\alpha]_D$ −29·8° ($c = 4{\cdot}6$).

l-Methylephedrine, prepared by addition of concentrated potassium hydroxide solution to a solution of *l*-methylephedrine hydrochloride in water, separated as an oil which rapidly solidified. It crystallised readily from methyl alcohol in stout needles, m. p. 87—88° (corr.). Previously recorded values are 59—62° (Miller, *Arch. Pharm.*, 1902, **240**, 481), 78° (Eberhard, *ibid.*, 1915, **253**, 65), 84° (Nagai, Abstract by Chen and Kao, *J. Amer. Pharm. Assoc.*, 1926, **15**, 632) (Found: C, 73·5; H, 9·4. Calc. for $C_{11}H_{17}ON$: C, 73·7; H, 9·6%). The base can be titrated with standard acid with methyl-red as indicator: 0·7956 g. required 44·4 c.c. of 0·1*N*-sulphuric acid. $C_{11}H_{17}ON$ requires 44·4 c.c. In methyl alcohol it had $[\alpha]_D$ −29·2° ($c = 3{\cdot}0$). When treated with methyl iodide in methyl-alcoholic solution, it gave a *methiodide* which crystallised from alcohol in stout tablets, m. p. 212—213° (corr.) and had $[\alpha]_D$ −21·8° ($c = 2{\cdot}9$) (Found: I, 39·6. $C_{12}H_{20}ONI$ requires I, 39·5%).

Methylation of l-*Ephedrine.*—*l*-Ephedrine (28·4 g.), dissolved in methyl alcohol (28·4 c.c.), was boiled on a water-bath, and methyl iodide (27 g.) in methyl alcohol (27 c.c.) was added slowly. The solution was boiled for 2 hours, concentrated under diminished pressure, and treated with potassium hydroxide solution and ether; 23·6 g. of the methiodide then separated. The alkaline liquor was

extracted with ether and added to the first ethereal extract. After drying over potassium carbonate, the ethereal solution was distilled, the residual base neutralised with aqueous oxalic acid, and successive crops of *l*-ephedrine oxalate, m. p. 249° (corr.), were removed. The final syrupy mother-liquor was treated with excess of potassium hydroxide solution; an oil then separated which rapidly solidified. It melted at 86—87° (corr.) after crystallisation from light petroleum and at 87—88° (corr.) after a further crystallisation from methyl alcohol. When mixed with the alkaloid obtained from Ma Huang, it showed no depression in m. p. (Found: C, 73·7; H, 9·4. Calc. for $C_{11}H_{17}ON$: C, 73·7; H, 9·6%). It had $[\alpha]_D$ −29·5° in methyl alcohol ($c = 4·5$).

The base was dissolved in ether and neutralised with hydrogen chloride. On crystallisation from alcohol the hydrochloride formed colourless tablets, m. p. 188—189° (Found: C, 61·4; H, 8·3; Cl, 16·4. Calc. for $C_{11}H_{17}ON,HCl$: C, 61·2; H, 8·4; Cl, 16·4%). It had $[\alpha]_D$ −29·8° in water ($c = 5·7$). There was no depression of the melting point after admixture with the hydrochloride obtained from Ma Huang.

l-Methylephedrine methiodide crystallises from alcohol in stout tablets, m. p. 212—213° (corr.) (Eberhard, *loc. cit.*, gave m. p. 204°). In aqueous solution it had $[\alpha]_D$ −21·3° ($c = 5·5$) (Found: I, 39·3. Calc. for $C_{12}H_{20}ONI$: I, 39·5%).

l-*Methylephedrine picrate* was prepared by adding a solution of the hydrochloride to a saturated aqueous solution of picric acid. It crystallised readily from alcohol and melted at 144° (corr.) (Found: C, 50·3; H, 4·5. $C_{17}H_{20}O_8N_4$ requires C, 50·0; H, 4·9%).

Methylation of d-*ψ*-*Ephedrine.*—*d*-*ψ*-Ephedrine (56·8 g.), dissolved in methyl alcohol (56·8 c.c.), was boiled on a water-bath, and methyl iodide (56·8 g.) added slowly. The mixture was boiled for 4 hours and treated with potassium hydroxide solution and ether; it then deposited crystals of the methiodide (24·1 g.). The alkaline liquor was extracted with ether and the united ethereal extracts were dried over potassium carbonate. After removal of the ether a crystalline residue (47·6 g.) was obtained which was fractionally crystallised from light petroleum; it then gave as a first crop 6·7 g. of crude *d*-*ψ*-ephedrine, m. p. 113°. Subsequent crops of low-melting base were obtained which were found by titration to consist of nearly pure methylephedrine.

The base was converted into the hydrogen tartrate and purified by recrystallisation from water.

d-*ψ*-*Methylephedrine hydrogen tartrate* crystallises in needles which melt at 84° (corr.) and, after drying in a vacuum over sulphuric acid, at 152° (corr.) (Found in air-dried salt: loss in a vacuum over

H_2SO_4, 10·0. $C_{11}H_{17}ON,C_4H_6O_6,2H_2O$ requires loss, 9·9%. Found in dried salt: C, 54·6; H, 6·9. $C_{11}H_{17}ON,C_4H_6O_6$ requires C, 54·7; H, 7·0%).

d-*ψ*-*Methylephedrine* was prepared by the addition of sodium hydroxide solution to a solution of the hydrogen tartrate in water. The base was extracted with ether and dried over potassium carbonate, and the ether removed by distillation. The residue crystallised readily on cooling and melted at 29—30° (corr.). Emde (*Arch. Pharm.*, 1906, **244**, 246) obtained the base as a thick oily liquid. It was recrystallised from light petroleum at −10°; thereafter it melted at 30° (corr.). d-*ψ*-*Methylephedrine* is readily soluble in the common organic solvents, and somewhat sparingly soluble in water (Found: C, 73·7; H, 9·4. $C_{11}H_{17}ON$ requires C, 73·7; H, 9·6%). In methyl alcohol it had $[\alpha]_D$ +48·1° ($c = 4·7$). It can be titrated with standard acid and methyl-red: 0·6689 g. required for neutralisation 37·2 c.c. of 0·1*N*-sulphuric acid. $C_{11}H_{17}ON$ requires 37·3 c.c.

d-*ψ*-Methylephedrine methiodide crystallises readily from alcohol; m. p. 216—217° (corr.) (Emde, *loc. cit.*, gave m. p. 205°) (Found: I, 39·4. Calc. for $C_{12}H_{20}ONI$: I, 39·5%). In aqueous solution it had $[\alpha]_D$ +34·7° ($c = 2·9$).

d-*ψ*-*Methylephedrine picrate* was prepared by addition of a solution of the hydrochloride to a saturated solution of picric acid in water. It crystallised readily from alcohol and melted at 152—153° (corr.) (Found: C, 50·4; H, 4·9. $C_{17}H_{20}O_8N_4$ requires C, 50·0; H, 4·9%).

The author's thanks are due to Mr. W. Ramsay for assistance in this investigation.

WELLCOME CHEMICAL WORKS,
DARTFORD.

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CCLXXI.—*The Use of Titanous Chloride in the Volumetric Estimation of Copper and Iron.*

By WILLIAM GIDLEY EMMETT.

IN the course of a research involving many analyses of cupric chloride solutions, copper was estimated in the solutions by titration with titanous chloride, ferric ammonium sulphate in known quantity and potassium thiocyanate in excess being added as indicator. The method is well known and is described by Knecht and Hibbert ("New Reduction Methods in Volumetric Analysis," 1918) and other workers.

A source of error, apparently hitherto unremarked, lies in the

somewhat rapid decomposition of ferric and cupric thiocyanates by water at the ordinary and at higher temperatures. These reactions were investigated by Philip and Bramley (J., 1913, **103**, 795; 1916, **109**, 597), who showed that the salts were reduced; in the case of the ferric salt, the rate of reduction was diminished by acid when an excess of alkali thiocyanate was present, and greatly increased by a rise in temperature; but the rate of reduction of cupric thiocyanate was not investigated. The results of a brief study of these sources of error, in so far as they concerned the other research, are now reported.

The titrations were carried out according to the technique described by Knecht and Hibbert, carbon dioxide being passed through the flask. A 15% solution of titanous chloride, after being boiled with concentrated hydrochloric acid, was diluted to give an approximately 0·02*N*-solution, and stored in the apparatus depicted (*loc. cit.*). (The diluted solution contained as impurity about 0·00013 g. of iron per c.c. as determined by oxidising 5 c.c. of the original 15% solution with acidified potassium permanganate and titrating the resulting ferric salt with a standardised titanous chloride solution.) A solution of standardised (approx. 0·025*N*) acidified ferric ammonium sulphate was used for checking the titanous chloride solution before and after each series of titrations, a slight but continuous decline in strength being noted.

Decomposition of Ferric Thiocyanate.—Solutions of ferric thiocyanate, prepared by mixing 25 c.c. of ferric chloride solution of known strength with 10 c.c. of 10% potassium thiocyanate (A.R.), containing different quantities of hydrochloric acid were titrated with standard titanous chloride at various intervals after mixing. The results (Table I) show that the decomposition is slight at the

TABLE I.

Conc. of $Fe(CNS)_3$, *N*.	Acidity due to added HCl, *N*.	Temp.	Interval between mixing and titration (mins.).	Ferric salt reduced, %.
0·0184	nil	16°	3	<0·2
			6	0·5
			10	0·5
0·0184	nil	25	6	1·4
0·0189	nil	50	*ca.* 0·5	4·7
			1·5	11·5
			3	16·1
0·0189	0·43	50	*ca.* 0·5	1·7
			1·5	8·4
			3	12·9
*0·155	nil	25	12	5·1
			46	7·5
*0·155	0·25 (H_2SO_4)	25	15	2·5
			50	3·6

* Experiments by Philip and Bramley.

ordinary temperature, and (in agreement with Philip and Bramley) that it is more pronounced at higher temperatures, but is inhibited by acid. Consequently, in analytical work the titration of ferric thiocyanate solutions must be carried out at the ordinary temperature in the presence of free acid and without undue delay after addition of thiocyanate to the ferric salt.

Decomposition of Cupric Thiocyanate.—Titrations with titanous chloride after different intervals were made on portions of 25 c.c. of cupric chloride solution (A.R.) to which had been added as indicator 10 c.c. of 10% potassium thiocyanate (A.R.) and 5 c.c. of the standard ferric solution together with varying amounts of hydrochloric acid. Typical results are given in Table II.

TABLE II.

Conc. of $Cu(CNS)_2$, *N*.	Acidity due to added HCl, *N*.	Temp.	Interval between mixing and titration (mins.).	Cupric salt reduced, %.*
0·0151	Nil	16°	*ca.* ½	3·8
			2	6·6
			4	8·0
0·0144	0·09	Room temp.	2	<0·1
			6	0·7
0·0151	*ca.* 1·2	Room temp.	2½	0·2
			71	1·3

* Since the velocity of change of ferric thiocyanate at the ordinary temperature is seen to be small compared with that of cupric thiocyanate, the total reduction has been ascribed to the latter.

Solutions of cupric chloride containing hydrochloric acid in concentrations from 0·25*N* to 3·3*N*, when titrated at the ordinary temperature with titanous chloride as soon as possible after addition of potassium thiocyanate, gave results which agreed amongst themselves within 0·1%. It is thus seen to be essential in the titration of cupric thiocyanate solutions to observe the same precautions as in the case of ferric thiocyanate.

When solutions of cupric chloride (*ca.* 0·015*N*) and 10% potassium thiocyanate (with or without added acid) were mixed and kept for 10 minutes or more before titration with titanous chloride, sharp end-points were not obtained; after the red colour of the ferric thiocyanate indicator had yielded to a colourless solution holding a pale grey precipitate, it developed again in a few seconds. Further addition of a drop of titanous chloride caused decoloration followed by renewed appearance of colour, and so on. The phenomenon is ascribed to the precipitation of cupric thiocyanate from the solution while awaiting titration, black acicular crystals having been observed under such conditions; in the course of the titration the precipitate slowly redissolves and reacts at the end to re-form ferric thiocyanate.

This supplies another reason why titration of cupric thiocyanate solutions should be done without loss of time.

By following Knecht and Hibbert's method with the addition of the precautions mentioned, analyses with an error of less than 0·2% were easily obtained. The titanous chloride solutions were standardised against a solution of cupric chloride (A.R.) in which the chlorine had been determined gravimetrically as silver chloride and/or the copper as cuprous thiocyanate.

A more convenient method of preparing a standard copper solution consists in dissolving a known weight of electrolytic copper in a solution of sodium peroxide in hydrochloric acid. About 5 g. of sodium peroxide are added to about 20 c.c. water and the solution is acidified with concentrated hydrochloric acid, being kept cool meanwhile. About 1 g. of pure copper turnings is added and dissolves in about ½ hour. The solution is then boiled under reflux to decompose all hydrogen peroxide (or to drive off dissolved chlorine), and diluted to a convenient volume. This method gave results from 0·1 to 0·2% lower than that previously described, probably on account of the presence of traces of iron in the sodium peroxide used.

The use of ferrous ammonium sulphate as a primary standard has been adversely criticised by the U.S. Bureau of Standards (Circular No. 26, 1921, 11) and by Thornton and Wood (*Ind. Eng. Chem.*, 1927, **19**, 150), and the author's results are in agreement with this.

The reduction of solutions of cupric thiocyanate on standing gives a ready explanation of Tomiček's observation (*Rec. trav. chim.*, 1924, **43**, 798) that when copper sulphate solutions were titrated by the potentiometric method in the presence of an excess of potassium thiocyanate large divergences from the expected figures were obtained; his suggestion that the thiocyanate is changed to sulphide, the copper salt being thereby fixed, is probably incorrect.

Highly erratic results were also recorded by Mach and Lederle (*Landw. Versuchs-Stat.*, 1914, **84**, 142) when titrating mixtures of ferric chloride and cupric sulphate in the presence of potassium thiocyanate, the ascertained copper content of cupric sulphate crystals varying from 25·08 to 18·26% with increasing concentration of ferric salt, whilst analysis by the electrolytic method gave 25·52% copper. These vagaries may perhaps also be ascribed to decomposition of the thiocyanates prior to titration, or alternatively to precipitation of cupric thiocyanate from the solutions.

The author desires to express his indebtedness to Dr. S. R. Carter for valuable assistance in the course of the work.

THE UNIVERSITY OF BIRMINGHAM,
EDGBASTON.

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CCLXXII.—*Studies of Equilibria in the Systems Sodium Chloride–Lead Chloride–Water, Lithium Chloride–Lead Chloride–Water.*

By GEORGE E. R. DEACON.

THE purpose of this work was the investigation of those complex salts, if any, formed by lead chloride with sodium or lithium chloride, which are capable of existence in contact with aqueous solutions at 25°, and to obtain the isothermal diagrams for these systems.

The method used was the same as that described by Burrage

FIG. 1.

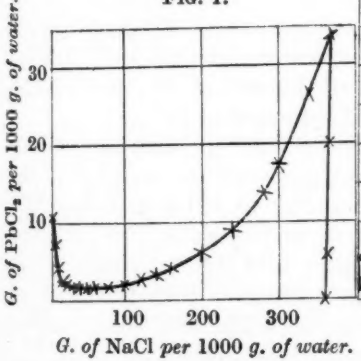
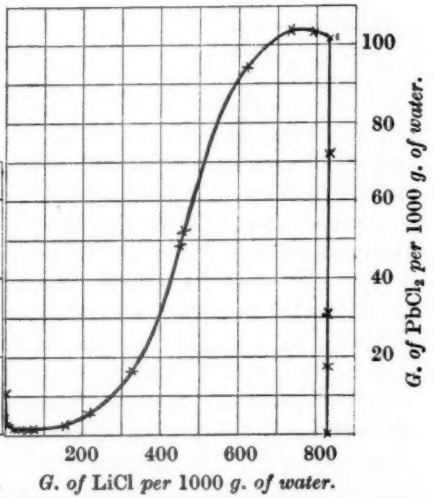


FIG. 2.



(J., 1926, 1703). The lead was estimated gravimetrically as chromate and the total chloride as silver chloride, water being found by difference. The analytical results for the liquid and wet solid phases were plotted on triangular diagrams according to Schreinemakers's method of residues; they exhibit the nature of the results more clearly, however, when plotted as in Figs. 1 and 2.

Lead Chloride–Sodium Chloride–Water.

Previous work on this system has led to conflicting results. (Mme.) Demassieux (*Ann. Chim.*, 1923, **20**, 233) studied the system at 100°, 50°, and 13°, and found that no double compounds existed. Kendall and Sloan (*J. Amer. Chem. Soc.*, 1925, **47**, 2306), working at 25°, describe the compound $2PbCl_2,NaCl$. The present investigation shows the absence of any such compound, the solid phases being lead chloride and sodium chloride only.

TABLE I (see Fig. 1).

Composition of the equilibrium solutions at 25° for the system $NaCl–PbCl_2–H_2O$. (Concentrations are expressed as g. per 1000 g. of water.)

NaCl.	$PbCl_2$.	Solid phase.	NaCl.	$PbCl_2$.	Solid phase.
—	10·87	$PbCl_2$.	143·0	3·52	$PbCl_2$.
5·0	7·24	,,	160·0	4·14	,,
8·8	4·22	,,	200·0	6·01	,,
15·57	2·52	,,	240·0	8·87	,,
20·0	2·09	,,	280·0	13·77	,,
30·0	1·80	,,	300·0	17·30	,,
40·0	1·72	,,	320·0	21·50	,,
50·0	1·67	,,	340·0	26·40	,,
60·0	1·75	,,	369·9	34·80	$PbCl_2$ + NaCl.
80·0	1·88	,,	367·0	20·10	NaCl.
100·0	2·14	,,	363·0	8·20	,,
121·0	2·79	,,	359·6	—	,,

Lead Chloride–Lithium Chloride–Water.

This system has been investigated at 50° by Demassieux (*loc. cit.*), and some measurements have also been made at 25° by Kendall and Sloan (*loc. cit.*), who claimed the existence of the salt $LiCl,2PbCl_2$. The present work shows the absence of this salt at 25°, and that of Demassieux shows that no compound is formed at 50°.

The system is singular in that the decrease in solubility of the lead chloride to 1·39 g. and the subsequent increase to 103·5 g. are followed by a slight decrease in solubility to 101·6 g. before the eutectic point is reached. The curve undergoes a break at the eutectic point, and a second solid phase $LiCl,H_2O$ separates. The separation of the monohydrate is in agreement with the work of Bogorodsky (*J. Russ. Phys. Chem. Soc.*, 1893, **25**, 316), who describes this hydrate as the stable form between 12·5° and 98°.

TABLE II (see Fig. 2).

Composition of equilibrium solutions at 25° for the system $LiCl–PbCl_2–H_2O$. (Concentrations are expressed as g. per 1000 g. of water.)

LiCl.	$PbCl_2$.	Solid phase.	LiCl.	$PbCl_2$.	Solid phase.
—	10·87	$PbCl_2$.	257·7	8·02	$PbCl_2$.
3·88	4·74	,,	329·2	16·36	,,
6·67	2·68	,,	453·9	48·71	,,
7·16	2·58	,,	458·8	52·34	,,
20·24	1·67	,,	621·8	94·43	,,
21·64	1·58	,,	735·2	103·5	,,
29·74	1·53	,,	794·1	103·4	,,
43·77	1·39	,,	834·9	101·6	$PbCl_2$ + $LiCl,H_2O$.
59·94	1·52	,,	835·0	72·0	$LiCl,H_2O$.
75·88	1·53	,,	835·0	31·0	,,
156·2	2·58	,,	830·0	17·2	,,
221·6	5·61	,,	830·5	—	,,

Treis (*Jahrb. Min. Beil.-Bd.*, 1914, **37**, 766), investigating the binary systems $PbCl_2$–XCl (where X = Li, Na, K, or Rb), found that whilst potassium gave two double compounds, and rubidium three, no combination was obtained between lithium or sodium chloride and lead chloride. Double salts are also formed between potassium and lead chlorides in aqueous solution (Burrage, *loc. cit.*).

Summary.

1. Equilibria existing at 25° in the systems NaCl–$PbCl_2$–H_2O, and LiCl–$PbCl_2$–H_2O have been investigated over the whole range of concentrations.

2. At this temperature, no double salts are capable of existence in either system.

The author desires to thank Professor Allmand, under whose direction this work was carried out during the session 1926—1927.

UNIVERSITY OF LONDON,
KING'S COLLEGE. [*Received, July 9th*, 1927.]

CCLXXIII.—*Ferric Thiocyanate.*

By KENNETH CLAUDE BAILEY.

IT is generally assumed that the blood-red substance produced by the interaction of ferric chloride and potassium thiocyanate, and extracted by ether from its aqueous solution, is ferric thiocyanate. Kruss and Moraht (*Ber.*, 1889, **22**, 2054) obtained double salts, to which they attributed the formulæ $9KSCN,Fe(SCN)_3,4H_2O$ and $3KSCN,Fe(SCN)_3,nH_2O$, by crystallisation from aqueous mixtures, but these salts were decomposed by moist ether, and could not account for the colour extracted by that solvent.

Clarens's suggestion (*Buli. Soc. chim.*, 1923, **33**, 988) that the substance obtained in presence of an excess of ferric chloride is a dithiocyanate has been combated by the author (*Proc. Roy. Irish Acad.*, 1924, **37**, *B*, 2, 6).

Tarugi stated (*Gazzetta*, 1904, **34**, ii, 326; *Annali Chim. Appl.*, 1925, **15**, 416; 1926, **16**, 281) that the red compound was a per oxidised ferrous salt, $FeHC_3N_3S_3O_3$, but his conclusions from hi earlier work were disputed by Bongiovanni (*Gazzetta*, 1907, **37**, i, 472). Although Tarugi reaffirmed these conclusions in his later work, it was deemed desirable to repeat his experiments and examine point by point the most striking arguments which he adduced in support of his formula.

According to his directions, therefore, an excess of freshly prepared ferric hydroxide was dissolved in aqueous thiocyanic acid, the solution saturated with sodium chloride and extracted with ether, and the extract filtered and dried, where desirable, over anhydrous sodium sulphate. The results obtained were identical with those given by an ethereal extract of ferric chloride and potassium thiocyanate (excess).

(1) A little of the fresh ethereal solution was added to water, and then gave a deep blue colour with potassium ferrocyanide and only a yellow colour with ferricyanide (Tarugi obtained a greenish colour and a blue colour, respectively). After being kept for some time, the solution gave a blue colour with ferricyanide, showing slow reduction of part of the iron to the ferrous condition.

(2) When dilute nitric acid was added to a strong solution of potassium thiocyanate, and the mixture shaken with ether, a red extract was obtained which was strongly acid. This result can hardly be attributed to oxidation as asserted by Tarugi, for a similar extract was obtained when hydrochloric acid was substituted for nitric acid, and the substance extracted was almost certainly thiocyanic acid (compare Bailey, *loc. cit.*; Werner and Bailey, J., 1926, 2970).

(3) A solution of ferric sulphate was prepared containing 5·58 g. per litre of iron and excess of acid. If no excess acidity had been present, 30 c.c. of $N/10$-sodium hydroxide should have sufficed to precipitate all the iron in 10 c.c. and give a neutral solution. About 69 c.c. were actually needed; 10 c.c. of the ferric solution contained, therefore, the equivalent of about 39 c.c. of $N/10$-acid in excess. When similar titrations were performed with solutions containing potassium thiocyanate and potassium oxalate, very indefinite results were obtained by the use of phenolphthalein, the indicator employed by Tarugi. Neutral litmus paper gave consistent results and was employed throughout.

Another source of error lay in the fact that the iron was not completely precipitated from solutions containing thiocyanate and oxalate until a fair excess of alkali was present, and there was a danger of adsorption of the alkali by the precipitated hydroxide. To avoid this, the solution was boiled, and 68 c.c. of $N/10$-alkali were added. The solution was filtered, the filter-paper washed, and further alkali added to ensure complete precipitation. The solution was again filtered, and the solution and washings were back-titrated with $N/10$-sulphuric acid. This procedure was followed even in the case of the plain ferric sulphate solution, to ensure uniformity of results, for each filtration necessarily incurs loss. The following results were obtained:

10 C.c. of ferric sulphate solution required 69·1 c.c. of N/10-sodium hydroxide.

10 C.c. of ferric sulphate solution + 60 c.c. of N/10-potassium thiocyanate (*i.e.*, 6 mols.) required 69·3 c.c.

10 C.c. of ferric sulphate solution + excess of concentrated potassium thiocyanate + potassium oxalate until solution was pale yellow required 69·1 c.c.

No increase in free acidity due to the reduction of iron to the ferrous condition was observed, and the only plausible explanation of Tarugi's statement, that such increase occurs, is that an error was introduced by the use of phenolphthalein, or by adsorption of sodium hydroxide by the precipitate.

Tarugi suggested that the decolorisation of the red solution by potassium oxalate was due to reduction of the red peroxidised compound by the oxalate. If this were the case, an amount of potassium oxalate equivalent to the original red compound should be oxidised during the reaction.

Quantitative estimations showed that no oxalate disappeared during the operation, and that twenty times as much oxalate was necessary for approximate decolorisation as should have sufficed for reduction of the peroxidised compound supposed to be present. This result was consistent with the disappearance of the red colour by double decomposition, but not with reduction of a peroxidised compound at the expense of the oxalate.

(4) Some fresh, red, ethereal solution was decolorised by potassium oxalate. Ammonia was added and the precipitate was quickly filtered off, washed with air-free water, and dissolved in hydrochloric acid; the solution gave an intense blue colour and precipitate with ferrocyanide, but only a greenish-yellow solution with ferricyanide. Tarugi's result (that the iron is precipitated in the ferrous condition) is only intelligible on the supposition that the ferric oxalate solution was exposed to sunlight, which would probably cause formation of some ferrous oxalate.

(5) Some of the ethereal solution was treated with oxalate, calcium chloride, and ammonia, as directed by Tarugi. The precipitate, as before, contained ferric iron and no ferrous iron. To the neutralised filtrate one drop of very dilute ferric chloride solution was added. A red colour, readily extracted by ether, was produced. Tarugi obtained a red colour not extracted by ether. This result may be easily explained. If the solutions employed are fairly dilute, the filtrate is a very dilute solution of thiocyanate, and even one drop of concentrated ferric chloride produces an excess of the latter reagent. The red colour is then only extracted with diffi-

culty. By using concentrated solutions of the other reagents and a dilute solution of ferric chloride, a mixture is obtained in which the thiocyanate is in excess, and the colour is readily extracted (see Durand and Bailey, *Bull. Soc. chim.*, 1923, **33**, 653; Bailey, *loc. cit.*).

(6) To water freed from air by boiling, some ammonia was added in a separating funnel, and red ethereal solution till the funnel was quite full. After shaking, the precipitate was allowed to subside, and had the typical appearance of ferric hydroxide; it was rapidly and repeatedly washed with air-free water, and dissolved in a little acid. The resulting solution gave no blue colour with ferricyanide. The supernatant liquid was tested for thiocyanate as under (5), with similar results.

(7) The ethereal solution gave a blue colour with benzidine, but a similar result was obtained with ferric chloride and benzidine. This reaction, therefore, does not prove the peroxidised nature of the red compound.

(8) An attempt was made to crystallise the red compound from its ethereal solution, dried over anhydrous sodium sulphate. This solution, however, when kept in a desiccator, changed in composition even before depositing solid, and a solution which originally gave only a yellow colour with ferricyanide soon gave a blue colour, showing conversion of iron into the ferrous state. After the solution had evaporated almost completely, the residue remained moist for about a week. This red liquid was acid in reaction, and doubtless contained free thiocyanic acid. A large proportion of the iron in the solid residue, although not all, was in the ferrous condition.

Philip and Bramley (J., 1913, **103**, 795) observed reduction of ferric thiocyanate in aqueous solution:

$$8Fe(CNS)_3 + 6H_2O = 8Fe(CNS)_2 + 7HCNS + CO_2 + H_2SO_4 + NH_3.$$

It seems possible that a similar reduction of ferric thiocyanate to ferrous thiocyanate with production of thiocyanic acid is taking place here. In view of the undoubted and rapid alteration of the red product, it seems unlikely that an analysis of any substance crystallised from the ethereal solution in a desiccator (Tarugi found Fe, 20·59; S, 34·37. Calc. for $FeHC_3N_3S_3O_3$: Fe, 20·07; S, 34·40%) can give results sufficiently trustworthy to establish a formula such as that proposed by Tarugi.

Summary.

Many of the experiments described by Tarugi have been carefully repeated. No evidence was obtained to support his conclusion that the red compound formed by dissolving ferric hydroxide in an

aqueous solution of thiocyanic acid is $FeHC_3N_3S_3O_3$. The results all indicate that the compound is ferric thiocyanate.

The author wishes to express his gratitude to Professor E. A. Werner for the helpful interest which he has taken in this work.

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CCLXXIV.—*The Inflammation of Mixtures of the Paraffins and Air in a Closed Spherical Vessel.*

By GEORGE BARTON MAXWELL and RICHARD VERNON WHEELER.

IN a previous paper on the inflammation of mixtures of methane and air in a closed spherical vessel (J., 1918, **113**, 840), ignition being at the centre, it was recorded that the maximum pressures developed were about 10% less than the calculated values. For the calculations, the degree of dissociation of the products when inflammation had spread through the vessel was determined by analyses of samples rapidly withdrawn at the moment of attainment of maximum pressure; and Langen's values for specific heats were used. Close agreement between results obtained for mixtures of the same composition, inflamed within spheres of 4 and 16 litres capacity, showed that losses due to conduction of heat could not entirely account for the low experimental values, which were ascribed mainly to radiation losses. Experiments by Tizard and Pye (Empire Motor Fuels Committee, Report, 1923—24) with internal-combustion engines, gave surprisingly high results for the pressures produced on explosion of mixtures of heptane and air, the observed pressures being but little less than those calculated. Either the heat loss during the inflammation of heptane is considerably less than with methane, or the method of calculating explosion-temperatures used by Tizard and Pye gave low values.

The work herein described was undertaken to elucidate this matter and to study the factors which influence the rate of inflammation of hydrocarbons. The hydrocarbons used were the first five members of the paraffin series. Save that the pressure-gauge was fitted with a stronger spring than in the earlier determinations, the explosion-vessel (a 4-litre sphere) and the method of experiment were as described previously (*loc. cit.*). To ensure strictly comparable results throughout the series, the experiments with methane and ethane (see J., 1919, **115**, 81) were repeated. The pressures measured were slightly higher than in the earlier records, but the results, given in the tables that follow, did not otherwise differ

materially. Each table of observed results is followed by calculations of the maximum temperatures attainable and the theoretical maximum pressures for a number of mixtures. The method of calculation, which is explained in the experimental portion of the paper, was based on that used by Tizard and Pye (*loc. cit.*), whose data we have employed. The theoretical composition of the products of combustion of each mixture, and the ratios of the number of molecules present at the moment of maximum temperature to the initial number ("molecular ratios") are also recorded. All the mixtures were at an initial temperature and pressure of 15° and 1 atmosphere, and were ignited at the centre of the sphere.

TABLE I.

Mixtures of Methane and Air.

Theoretical mixture for complete combustion: 9·47% CH_4.
Approximate limits of inflammability: 5·6—13·6% CH_4.

Methane, %.	Time from ignition to first indication of press. (sec.).	Time from ignition to maximum press. (sec.).	Maximum press. above atmospheric (atm.).
6·05	0·167	0·545	2·67
6·40	0·122	0·340	3·80
7·15	0·076	0·151	5·08
7·35	0·058	0·119	5·69
8·30	0·025	0·081	6·63
8·60	0·025	0·078	6·91
9·15	0·031	0·070	7·21
9·65	0·021	0·069	7·35
9·70	0·031	0·068	7·37
10·20	0·020	0·067	7·43
10·40	0·038	0·068	7·28
10·80	0·021	0·071	7·21
11·40	0·040	0·087	6·88
11·90	0·045	0·102	6·54
12·10	0·041	0·137	6·41
12·70	0·071	0·257	5·35
13·40	0·166	0·368	4·23

Calculated Maximum Temperatures and Pressures.

CH_4, %.	Products of combustion * at moment of maximum temperature, %.						"Molecular ratio."	Maximum temp.	Press. rise, atm.
	CO_2.	CO.	H_2O.	H_2.	O_2.	N_2.			
7·00	6·70	0·17	15·40	0·05	5·46	72·22	1·0005	2005°	6·90
8·00	7·27	0·56	17·21	0·14	3·54	71·28	1·0010	2155	7·48
9·00	7·37	1·41	18·87	0·39	1·85	70·11	1·0072	2265	7·88
9·47	7·21	1·98	19·47	0·58	1·28	69·48	1·0130	2300	8·04
9·70	7·00	2·42	19·80	0·65	0·92	69·21	1·0135	2310	8·10
10·00	6·79	2·87	20·20	0·77	0·69	68·68	1·0185	2320	8·17
11·00	5·52	4·93	20·70	1·72	0·13	67·00	1·0275	2275	8·10
12·00	4·03	7·15	20·68	3·30	0·01	64·83	1·0550	2185	8·00
13·00	2·30	9·30	20·02	6·20	Trace	62·18	1·0934	2050	7·82

* CH_4 = nil.

TABLE II.

Mixtures of Ethane and Air.

Theoretical mixture for complete combustion : 5·64% C_2H_6.
Approximate limits of inflammability : 3·1—10·7% C_2H_6.

Ethane, %.	Time from ignition to first indication of press. (sec.).	Time from ignition to maximum press. (sec.).	Maximum press. above atmospheric (atm.).
4·10	0·056	0·113	6·34
4·45	—	0·097	6·70
4·90	0·039	0·076	7·36
5·15	0·035	0·066	7·39
5·55	0·030	0·055	7·62
6·15	0·024	0·050	7·87
6·30	0·024	0·052	7·94
6·75	0·029	0·056	7·81
6·95	0·034	0·060	7·89
7·50	0·037	0·083	7·42
7·60	0·051	0·088	7·35
8·20	0·078	0·172	6·94

Calculated Maximum Temperatures and Pressures.

C_2H_6, %	Products of combustion * at moment of maximum temperature, %.						"Molecular ratio."	Maximum temp.	Press. rise, atm.
	CO_2.	CO.	H_2O.	H_2.	O_2.	N_2.			
4·00	7·52	0·18	13·18	0·04	5·96	73·12	1·0269	1990°	7·04
4·80	8·34	0·84	15·24	0·17	3·48	71·93	1·0288	2210	7·88
5·20	8·37	1·51	16·20	0·26	2·43	71·23	1·0347	2280	8·18
5·80	8·05	2·83	17·38	0·57	1·17	70·00	1·0463	2350	8·51
6·00	7·79	3·42	17·68	0·76	0·86	69·49	1·0515	2355	8·59
6·20	7·54	4·01	18·06	0·85	0·52	69·02	1·0561	2350	8·61
7·00	5·69	7·00	18·37	2·23	0·05	66·66	1·0824	2280	8·57
8·00	3·27	10·58	17·94	4·41	Trace	63·80	1·1481	2110	8·50

* C_2H_6 = nil.

TABLE III.

Mixtures of Propane and Air.

Theoretical mixture for complete combustion : 4·02% C_3H_8.
Approximate limits of inflammability : 2·2—7·3% C_3H_8.

Propane, %.	Time from ignition to first appearance of press. (sec.).	Time from ignition to maximum press. (sec.).	Maximum press. above atmospheric (atm.).
2·45	0·143	0·303	4·37
3·50	0·039	0·073	7·51
3·70	0·038	0·063	7·83
4·25	0·033	0·055	8·00
4·60	0·035	0·055	8·09
5·15	0·034	0·062	7·90
5·25	0·043	0·062	7·89
5·65	0·049	0·087	7·59
6·45	0·102	0·198	6·13

Calculated Maximum Temperatures and Pressures.

C_3H_8, %.	Products of combustion * at moment of maximum temperature, %. CO_2.	CO.	H_2O.	H_2.	O_2.	N_2.	"Molecular ratio."	Maximum temp.	Press. rise, atm.
2·5	7·16	0·04	11·25	0·01	7·59	73·95	1·0248	1850°	6·56
3·0	8·21	0·36	13·01	0·07	5·24	73·11	1·0317	2075	7·43
4·0	8·65	2·54	16·06	0·45	1·61	70·71	1·0551	2340	8·56
4·4	8·03	4·10	16·95	0·79	0·63	69·50	1·0693	2370	8·80
4·6	7·47	5·11	17·27	1·08	0·36	68·71	1·0790	2365	8·88
5·5	4·58	9·76	17·00	3·63	0·09	64·94	1·1345	2190	8·71
6·0	2·80	12·40	16·80	5·18	0·02	62·80	1·1813	2065	8·59

* C_3H_8 = nil.

TABLE IV.

Mixtures of Butane and Air.

Theoretical mixture for complete combustion: 3·12% C_4H_{10}.
Approximate limits of inflammability: 1·65—5·7% C_4H_{10}.

Butane, %.	Time from ignition to first appearance of press. (sec.).	Time from ignition to maximum press. (sec.).	Maximum press. above atmospheric (atm.).
2·05	0·078	0·149	5·20
2·55	0·043	0·078	7·42
3·00	0·027	0·059	8·15
3·60	0·027	0·055	8·48
3·70	0·029	0·054	8·33
3·75	0·027	0·057	8·59
4·40	0·041	0·080	7·78
4·75	0·081	0·117	7·18
4·85	0·061	0·127	7·03
5·15	0·136	0·221	5·83

Calculated Maximum Temperatures and Pressures.

C_4H_{10}, %.	Products of combustion * at moment of maximum temperature, %. CO_2.	CO.	H_2O.	H_2.	O_2.	N_2.	"Molecular ratio."	Maximum temp.	Press. rise, atm.
2·0	7·55	0·10	11·19	0·02	7·19	73·95	1·0301	1905°	6·80
3·0	8·89	2·26	15·16	0·36	2·03	71·30	1·0581	2330	8·56
3·5	7·94	4·77	16·59	0·87	0·51	69·32	1·0821	2380	8·95
3·7	7·20	6·09	16·79	1·38	0·20	68·34	1·0955	2355	9·00
4·5	2·76	12·24	16·28	5·11	0·01	63·60	1·2091	2020	8·62

* C_4H_{10} = nil.

The Pressures developed.—Comparison between the observed and the calculated pressures is made in Fig. 1. Both experiment and calculation show the maximum pressure to be given in each instance by a mixture containing an excess of hydrocarbon over that required for complete combustion. The amounts of these "displacements" are recorded in Table VI, together with the observed and calculated maximum pressures and the amounts of "lost pressure" expressed as % of the calculated values.

FIG. 1.

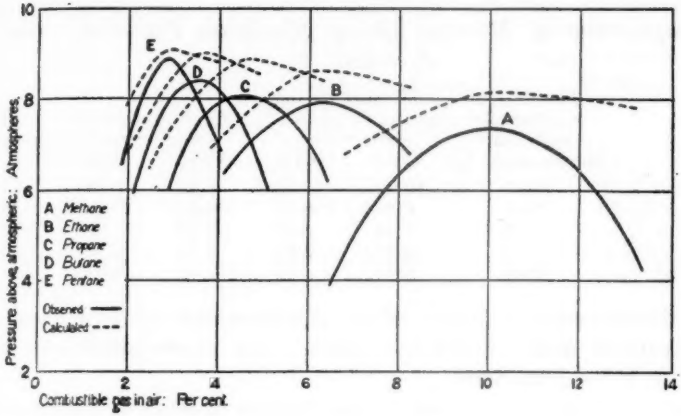


TABLE V.

Mixtures of Pentane and Air.

Theoretical mixture for complete combustion : 2·55% C_5H_{12}.
Approximate limits of inflammability : 1·35—4·5% C_5H_{12}.

Pentane, %.	Time for ignition to first appearance of press. (sec.).	Time for ignition to maximum press. (sec.).	Maximum press. above atmospheric (atm.).
1·95	0·057	0·110	6·65
2·05	0·056	0·089	7·54
2·30	0·045	0·071	7·80
2·40	0·044	0·069	8·10
2·70	0·038	0·059	8·74
2·80	0·024	0·056	8·93
3·00	0·030	0·059	8·87
3·15	0·033	0·064	8·77
3·45	0·037	0·065	8·09
3·60	0·063	0·099	7·91
3·85	0·076	0·021	7·58
4·10	0·113	0·191	6·97

Calculated Maximum Temperatures and Pressures.

C_5H_{12}, %.	Products of combustion * at moment of maximum temperature, %.						"Molecular ratio."	Maximum temp.	Press. rise, atm.
	CO_2.	CO.	H_2O.	H_2.	O_2.	N_2.			
2·0	8·82	0·62	12·88	0·09	4·56	73·03	1·0340	2155°	7·80
2·5	9·06	2·49	15·08	0·39	1·78	71·20	1·0645	2350	8·70
2·75	8·52	3·98	15·77	0·81	0·92	70·00	1·0799	2380	8·94
3·0	7·45	5·98	16·45	1·21	0·27	68·64	1·0985	2370	9·07
4·0	2·04	14·04	16·64	4·87	Trace	62·41	1·1959	2075	8·75

* C_5H_{12} = nil.

The close agreement in composition between the observed and calculated maximum-pressure mixtures leads to the conclusion that

TABLE VI.

Compositions of Mixtures giving Maximum Pressures. Lost Pressures, %.

	Theoretical mixture for complete combustion, %.	Mixture giving maximum press., %.		Maximum press.		Lost press., %.
		Calc.	Obs.	Calc.	Obs.	
Methane	9·47	10·00	10·00	8·18	7·38	9·80
Ethane	5·64	6·20	6·30	8·63	7·91	8·35
Propane	4·02	4·60	4·60	8·87	8·09	8·80
Butane	3·12	3·70	3·65	9·00	8·50	5·55
Pentane	2·55	3·00	2·95	9·07	8·85	2·45

the " displacements " are the effects of dissociation on the explosion-temperatures and " molecular ratios," for which allowance was made in the calculations.

The " lost pressure " may be due to loss of heat by conduction and radiation or to incomplete combustion. It was shown in a previous paper (*loc. cit.*) that, in mixtures of methane and air containing between 7·5 and 12·5% of methane, a loss of heat by conduction of 2—3% can be presumed during the attainment of uniformity of temperature after inflammation. Such a loss may be assumed also with the other hydrocarbons. It is not easy to obtain a comparison of radiation losses during combustion of each hydrocarbon from the calculated compositions of the products. The intensities of radiation from steam and from carbon dioxide have been determined by Julius (" Die Licht- und Warmestrahlung verbrannter Gase," Berlin, 1890) and R. von Helmholtz (" Die Licht- und Warmestrahlung verbrennender Gase," Berlin, 1890), but the most trustworthy figures seem to be those recorded by Haslam, Lovell, and Hunneman (*Ind. Eng. Chem.*, 1925, **17**, 272), who estimated (by measuring the radiation from flames of methane and carbon monoxide, the theoretical amount of primary air being used with each) that the intensity of radiation from steam was about 1·7 times that from carbon dioxide. If these results be accepted, a comparison can be made of the relative " radiating powers " of the mixtures of carbon dioxide and steam in the products of combustion of the different hydrocarbons. Such a comparison is made in Table VII. The figures in columns 2 and 3 give the relative numbers of molecules of carbon dioxide and steam calculated to be present in the products of combustion of each maximum-pressure mixture at the moment of maximum pressure. These values were obtained from Tables I—V by multiplying the respective volume percentages by the corresponding molecular ratio.

The radiating power thus decreases from the methane to the pentane mixture, which is in accord with the decrease in " lost

TABLE VII.

Relative Radiating Powers of Products of Combustion of Maximum-Pressure Mixtures.

Mixture.	CO_2, g.-mols.	H_2O, g.-mols.	Ratio, H_2O/CO_2.	Relative radiating power. (CO_2% + 1·7 H_2O %.)
CH_4, 10·0%	0·0691	0·2058	2·98	41·8
C_2H_6, 6·2%	0·0796	0·1907	2·40	40·3
C_3H_8, 4·6%	0·0806	0·1863	2·31	39·7
C_4H_{10}, 3·7%	0·0789	0·1838	2·33	39·1
C_5H_{12}, 3·0%	0·0818	0·1808	2·21	38·9

pressure" (Table VI). It must be borne in mind, however, that the calculated maximum explosion-temperature rises from the methane to the pentane mixture, which would offset the decreasing H_2O/CO_2 ratio because of the difference in the mean wave-lengths of the radiations. It is, on the whole, improbable that differences in radiation loss account entirely for the differences in "lost pressure."

A more probable explanation lies in errors in the values for specific heats (Bjerrum, *Z. Elektrochem.*, 1911, **17**, 731; 1912, **18**, 101) on which our calculations, as also Tizard and Pye's, were based. Recent work by Womersley (*Proc. Roy. Soc.*, 1921, *A*, **100**, 483) suggests that Bjerrum's values for steam at high temperatures were much too low. Womersley's results extend only to 2000°, and for calculations of explosion-temperatures higher than this figure extrapolated values must be used. A few calculations are recorded in Table VIII, and if they are compared with those given in Table I, it will be seen that the composition of the mixture for which the calculated pressure is greatest (10% methane) is unchanged, but that the value for the pressure, 7·59 as compared with 8·17 atm., is considerably lower when Womersley's figures are used. The calculated pressure is, in fact, very near that found

TABLE VIII.

Calculated Maximum Temperatures and Pressures on Explosion of Methane–Air Mixtures.

(Based on Womersley's values for the specific heat of steam.)

CH_4 in original mixture, %	Products of combustion * at moment of maximum temperature, %.						"Molecular ratio."	Maximum temp.	Press. rise, atm.
	CO_2.	CO.	H_2O.	H_2.	O_2.	N_2.			
9·8	7·80	1·71	20·12	0·58	0·42	69·37	1·0112	2160°	7·54
10·0	7·52	2·16	20·35	0·70	0·30	68·98	1·0145	2165	7·59
10·2	7·25	2·62	20·56	0·81	0·13	68·63	1·0174	2150	7·57

* CH_4 = nil.

experimentally (7·38 atm.). No doubt the true value for the mean specific heat of steam over the range 100—2000° lies between

Bjerrum's (8·42 cals. per g.-mol.) and Womersley's (11·69). If so, calculations of maximum explosion-temperatures based on Bjerrum's figures would be too high, and the amount of the error would increase with the amount of steam in the products of combustion. Values for the amounts of steam in the products of combustion of unit volume of the maximum-pressure mixture for each hydrocarbon at the moment of maximum pressure are given in Table VII, from which it appears that over-estimation of loss of pressure would be greatest with methane and least with pentane (see Table VI).

There may also be error in the values (from Nernst, *Z. anorg. Chem.*, 1905, **45**, 130; and Bjerrum, *Z. physikal. Chem.*, 1912, **79**, 513) used in estimating the amount of dissociation of carbon dioxide and steam. In this connexion, it is of value to compare the analyses of samples of the gases rapidly withdrawn from the explosion-vessel at the moment of maximum pressure with methane–air mixtures (J., 1918, **113**, 840) with the calculated compositions of the products of combustion of similar mixtures (Table IX).

TABLE IX.

Observed and Calculated Compositions of Products of Combustion, %.

CH_4 in original mixture,	CO_2,		CO,		H_2,		O_2,		CH_4,
%	obs.	calc.	obs.	calc.	obs.	calc.	obs.	calc.	obs.*
7·90	9·25	7·21	0·15	0·49	Nil	0·11	3·82	3·72	Nil
9·40	11·14	7·20	0·26	1·96	,,	0·50	0·74	1·31	,,
9·90	10·66	6·84	1·12	2·74	0·40	0·77	0·13	0·77	0·24
10·00	10·86	6·79	1·08	2·87	0·68	0·77	0·04	0·69	0·04
10·70	9·04	5·95	3·63	4·30	2·21	1·40	Nil	0·24	0·10
11·05	9·00	5·45	3·44	5·00	1·95	1·77	,,	0·13	0·23
12·10	8·09	3·84	5·85	7·30	4·00	3·46	0·07	0·01	0·07
12·90	6·08	2·51	7·78	9·02	6·73	5·80	0·05	Nil	0·36
13·90	5·45	0·84	8·95	11·50	9·45	9·50	Nil	,,	1·00

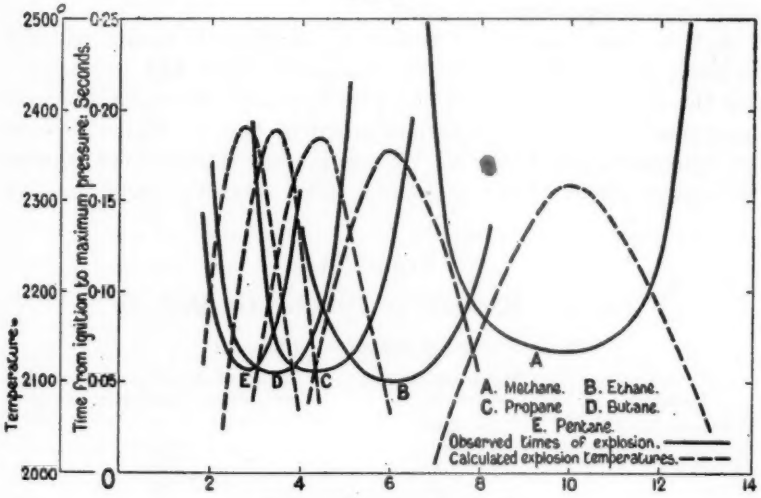
* "Calc. = nil."

There is an indication from these results that the extent of the dissociation of carbon dioxide has been over-estimated in the calculations, for the experimental values for the amounts of this gas in the products of combustion at the moment of maximum pressure are consistently high. In part, the discrepancy might be due to recombination during cooling of the samples (which was, however, very rapid), but this is not likely in view of the close agreement of the observed and calculated figures for hydrogen. Further, Fig. 1 shows that the discrepancy between observed and calculated pressures is greatest for mixtures containing an excess of combustible gas, a result which can be attributed to over-estimation of the "molecular ratios" in the calculations. It would thus seem that the decrease in "lost pressure" in passing from methane to pentane

(Table VI) may be more apparent than real. It is probable that the unexpectedly close agreement between calculated and observed engine efficiencies with heptane as fuel, recorded by Tizard and Pye, was also due to errors in the data on which the calculations were based.*

The Rate of Development of Pressure.—With a given hydrocarbon, it is apparent that the main factor controlling the mean rate of pressure development on explosion of its mixtures with air is the mean temperature of explosion. This is clear from Fig. 2, in which the effect of variation in composition of the mixtures on the rate of development of pressure is shown graphically for each hydro-

FIG. 2.



carbon, together with the calculated explosion-temperatures. Table X has been compiled from Fig. 2, and makes comparison between the observed "maximum-speed" mixtures and the calculated "maximum-temperature" mixtures. The "maximum-speed" mixture for each gas is that in which the time from ignition to the attainment of maximum pressure is least.

As a corollary to the observation that, under the conditions of these experiments, the mean rate of pressure development with a given paraffin is determined by the mean explosion-temperature, it follows that the "displacement" of the maximum-speed mixture

* Fenning and Tizard have recently published a paper on the dissociation of carbon dioxide at high temperatures (*Proc. Roy. Soc.*, 1927, *A*, **115**, 318) which confirms our conclusion. (Added July 10th, 1927.)

TABLE X.

Composition of Maximum-speed and Maximum-temperature Mixtures.

	Hydrocarbon in maximum-speed mixture (obs.), %.	Hydrocarbon in maximum-temperature mixture (calc.), %.	Mean temp. (calc.).	Time (obs.) from ignition to maximum-pressure (sec.).
Methane	10·0	10·0	2320°	0·067
Ethane	6·05	6·0	2355	0·051
Propane	4·45	4·4	2370	0·055
Butane	3·50	3·45	2380	0·055
Pentane	2·90	2·8	2380	0·057

is due to the same cause, dissociation, as displaces the calculated maximum-temperature mixture.

In this connexion, it is of interest to compare the results recorded in Table X with Mason's determinations (J., 1923, **123**, 210) regarding the mixture of each of the paraffins with air which gave the maximum speed of uniform movement of flame. Mason's results are summarised in Table XI. There is general agreement between the compositions of the maximum-speed mixtures under the two

TABLE XI.

Uniform Movement in Paraffin–Air Mixtures.

	Maximum-speed Mixtures. (Mason.)	
Paraffin.	Maximum-speed mixture, %.	Speed of uniform movement (5-cm. diam. tube) (cm. per sec.).
Methane	9·65	91
Ethane	6·05	127
Propane	4·45	114
Butane	3·65	113
Pentane	2·90	115

different conditions of experiment, and the order of speed of flame in the series of mixtures is the same. This is in accord with our recent observation (this vol., p. 297) that the generalisation known as "the law of speeds," first formulated with respect to the uniform movement of flame, applies also to the rate of spread of flame within a closed sphere.

EXPERIMENTAL.

The explosion-vessel and its fittings have been described in J., 1918, **113**, 854. Ignition of the mixtures was at the centre of the vessel by a secondary discharge from a "10-inch" induction-coil at a 1 cm. gap between pointed copper electrodes, the current through the primary circuit being 10 amps. and the trembler of the coil being locked.

The pressure-gauge was calibrated by compressed air at intervals during the series of experiments against a standard Bourdon gauge. The mean of the calibrations, which checked well amongst themselves, showed a deflexion of the manometer stylus of 1 cm. for a pressure increase of 7·85 atm.

The hydrocarbons were obtained as follows: Methane, from a blower of fire-damp in S. Wales; ethane, (*a*) by the action of water on zinc ethyl, or (*b*) from a cylinder of the compressed gas obtained (from America) by the fractionation of natural gas; propane and butane, by the action of the zinc–copper couple on the corresponding alkyl iodide in alcoholic solution; pentane, from a petroleum distillate, b. p. 35—40°. Each gas, after purification by washing with suitable solvents, was twice liquefied, the middle-boiling fraction only being retained. The ratios C/A (C = contraction on explosion analysis; A = subsequent absorption by potassium hydroxide solution) were: Methane, 1·995; ethane, (*a*) 1·253, and (*b*) 1·245; propane, 1·003; butane, 0·878; pentane, 0·804.

Each gas mixture was prepared in a 20-litre glass gas-holder over a dilute solution of potassium hydroxide and was analysed before use. Before an experiment, the explosion-vessel was exhausted of air to within a few mm. of mercury, filled with the mixture required, re-exhausted and filled again.

Calculation of Explosion Temperatures and Pressures.—The explosive mixtures were assumed to be saturated with water vapour at 15° and the analyses (which take no account of water vapour) were adjusted accordingly. The analytical figures were then proportional to the numbers of molecules of each constituent present in unit volume, and to their partial pressures.

In unit volume of the products of explosion, the numbers of molecules of the constituents can be expressed by $a\ CO_2 + b\ CO + c\ H_2O + d\ H_2 + e\ O_2 + f\ N_2$.

The ratio of the total number of molecules per unit volume at the moment of maximum temperature to the total number in unit volume of the original mixture (the "molecular ratio," M) is $(a + b + c + d + e + f)/1$. The partial pressure of, say, carbon dioxide at the moment of maximum temperature is aP_e/M, whilst $P_e = MT_e/T_i$, where P_e is the explosion-pressure in atmospheres, and T_e and T_i are the explosion-temperature and the initial temperature in °K. For example, in a mixture of pentane and air containing in unit volume: C_5H_{12}, 0·0246; O_2, 0·2005; H_2O, 0·0170; N_2, 0·7579, there are only five unknowns, for the number of molecules of nitrogen, f, can be regarded as remaining constant. Five independent relationships are therefore required to determine them. By equating the carbon, oxygen, and hydro-

gen before and after explosion, the following relationships are obtained:

$$a + b = 5 \times 0{\cdot}0246 = 0{\cdot}1230 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(i)}$$

$$2a + b + c + 2e = 2 \times 0{\cdot}2005 + 0{\cdot}0170 = 0{\cdot}418 \quad . \quad \text{(ii)}$$

$$c + d \qquad = 6 \times 0{\cdot}0246 + 0{\cdot}0170 = 0{\cdot}1646 \, . \quad \text{(iii)}$$

The equilibrium constants, K_1 and K_2, can be obtained from Nernst's data, thus:

$$K_1 = \frac{P^2_{CO} \times P_{O_2}}{P^2_{CO_2}} = \frac{b^2 e}{a^2} \cdot \frac{T_e}{T_i}; \text{ whence } \frac{b^2}{a^2} e = K_1 \frac{T_i}{T_e} \quad . \quad . \quad \text{(iv)}$$

$$\text{and } K_2 = \frac{P_{CO} \times P_{H_2O}}{P_{CO_2} \times P_{H_2}} = \frac{bc}{ad} \cdot \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(v)}$$

Expressions (iv) and (v) involve the explosion-temperature, T_e. A value for this is assumed and the equations are then solved. The simplest method of solution is to attribute different values to one of the unknowns, say e, until the relationship $bc/ad = K_2$ is satisfied.

From the solutions of the equations the rise in temperature can be calculated, since it represents the ratio between the thermal energy released on explosion of unit volume of the mixture and the thermal capacity of the products of explosion of unit volume. In the pentane–air mixture chosen as an example, the thermal energy released is that from 0·0246 g.-mol. of pentane less the calorific value of b g.-mol. of carbon monoxide and d g.-mol. of hydrogen. The thermal capacity of the products = amount of each constituent multiplied by its mean specific heat between 15° and the assumed explosion-temperature.

If the explosion-temperature so calculated does not agree within 5° of the predicted value, a fresh calculation is made with a new value for T_e. In the example given, the value for T_e finally chosen was 2618° K. and the calculated value then was 2623° K. The latter was accordingly taken as representing the maximum explosion-temperature. The molecular ratio was found to be 1·0645, so that the explosion-pressure, P_e, was $(2623/288) \times 1{\cdot}0645 = 9{\cdot}7$ atm. The pressure rise above atmospheric was therefore 8·70 atm.

The experiments described in this paper have been carried out for the Safety in Mines Research Board, to whom our thanks are due for permission to publish the results.

SAFETY IN MINES RESEARCH LABORATORIES,
SHEFFIELD. [*Received, May 11th*, 1927.]

CCLXXV.—*The Reduction of Nitro-compounds by Aromatic Ketols. Part I. Some* p-*Azoxy-compounds.*

By Hugh Bryan Nisbet.

That benzoin and its analogues may reduce Fehling's solution has been known for a long time, but the possibility of reducing nitro-groups by means of these agents has not hitherto been investigated. It has now been found that benzoin, anisoin, and furoin, in hot alcoholic solution in the presence of a trace of sodium methoxide or ethoxide, may be successfully used for the reduction of nitro-groups to azoxy-groups :

$$2R{\cdot}NO_2+3R{\cdot}CH(OH){\cdot}COR = R_2N_2O + 3R{\cdot}CO{\cdot}COR + 3H_2O.$$

The reduction is particularly successful in the case of *p*-nitro-compounds such as the *p*-nitrobenzylideneanilines, *p*-nitrobenzonitrile, the *p*-nitrocinnamic esters, and the *p*-nitrostilbenes, since the azoxy-compounds formed are, in general, sparingly soluble substances and may be readily separated from the 1 : 2-diketone to which the ketol is oxidised in the course of the reaction. The reduction proceeds very quickly, in some cases with ebullition of the solvent, and in a very short time the *p*-azoxy-compounds separate from solution. The 1 : 2-diketone may be recovered in each case from the mother-liquor.

With benzoin as reducing agent, 60—70% yields of *p*-azoxybenzylideneanilines can be obtained from the corresponding *p*-nitrobenzylideneanilines. *p*-Azoxybenzylideneaniline so obtained is identical with that obtained by reducing *p*-nitrobenzylideneaniline with alkali sulphides (*Chem. Zentr.*, 1900, ii, 612) or with alcoholic potash (Alway, *Ber.*, 1902, **35**, 2436), by treating *p*-nitrobenzyl chloride with caustic potash (Alway, *loc. cit.*), or by condensing *p*-azoxybenzaldehyde with aniline (Alway, *Amer. Chem. J.*, 1902, **28**, 43). *p*-Azoxybenzylidene-*p*-toluidine prepared by this method is identical with the compound prepared by reducing *p*-nitrobenzylidene-*p*-toluidine with alkali sulphides (*Chem. Zentr.*, 1900, ii, 612) or by the condensation of *p*-azoxybenzaldehyde with *p*-toluidine (Alway, *Ber.*, 1902, **35**, 2437). *p*-Nitrobenzylidene-*p*-aminoacetophenone is reduced by benzoin to *p*-azoxybenzylidene-*p*-aminoacetophenone.

Japp and Miller (J., 1893, **63**, 474) showed that benzoin and benzonitrile in the presence of concentrated sulphuric acid condense to form triphenyloxazole ; but *p*-nitrobenzonitrile is reduced by benzoin to *p*-azoxybenzonitrile.

By this method of reduction the esters of *p*-azoxycinnamic acid can be prepared directly from the esters of *p*-nitrocinnamic acid,

and the azoxy-acid can be obtained by hydrolysis. The yields of the reduction products are good, usually 70%, and the reaction proceeds very quickly, whereas the reduction of the nitro-acid electrolytically (Marie, *Comp. rend.*, 1905, **140**, 1248) or by sodium arsenite (Vorländer, *Ber.*, 1906, **39**, 806) and the formation of the esters of the azoxy-acid through the silver salt (Vorländer, *loc. cit.*) are all tedious methods.

p-Nitrostilbenes also are easily reduced by this method to *p*-azoxystilbenes, which may be obtained in excellent yield. The table gives the *p*-azoxystilbenes prepared by this method, the approximate yield, usually the average of two experiments, and the molecular weights of those compounds which are sufficiently soluble in 2 : 4-dinitrotoluene to allow of the determination by the cryoscopic method in that solvent (Auwers, *Z. physikal. Chem.*, 1899, **30**, 310).

Azoxy-compounds.	Yield.	*M*, found.	*M*, calc.
p-Azoxystilbene	70%	396	402
p-Azoxy-2-nitrostilbene	70%	487	492
p-Azoxy-2 : 3′-dinitrostilbene	45%	—	—
p-Azoxy-2 : 6-dinitrostilbene	Small	—	—
p-Azoxy-2-nitro-4′-methoxystilbene	70%	512	552
p-Azoxy-2-nitro-3′ : 4′-methylenedioxystilbene	65%	586	580
p-Azoxy-2 : 6-dinitro-4′-methoxystilbene	45%	—	—
p-Azoxy-2-nitro-4′-dimethylaminostilbene	42%	—	—

Anisoin and furoin were substituted for benzoin in the reduction of 2 : 4-dinitrostilbene and gave approximately the same yield of the same azoxy-compound. The mother-liquors yielded anisil and furil, respectively. In all the reductions in which benzoin was used, benzil was recovered from the mother-liquors.

Experimental.

Preparation of Nitrostilbenes.—A modification of Bishop and Brady's method (J., 1922, **121**, 2367) was used. A solution of the polynitrotoluene and the aromatic aldehyde in molecular proportion and 1 c.c. of piperidine in a small quantity of benzene is boiled under reflux until the reaction is complete, the time varying from 1 to 6 hours. The benzene is then allowed to evaporate and the crystalline mass is washed with benzene–light petroleum and recrystallised from glacial acetic acid. 2 : 4-Dinitro-4′-methoxystilbene, 75% yield, m. p. 163° (compare Pfeiffer, *Annalen*, 1916, **411**, 91). 2 : 4 : 3′-Trinitrostilbene, 50% yield, m. p. 182—183° (compare Pfeiffer, *loc. cit.*). 2 : 4 : 4′-*Trinitrostilbene*, from 2 : 4-dinitrotoluene (9 g.) and *p*-nitrobenzaldehyde (7·5 g.). Yield, 12 g. Dark orange needles, m. p. 234—235° (Found: C, 53·9; H, 3·0. $C_{14}H_9O_6N_3$ requires C, 53·3; H, 2·9%). 2 : 4-*Dinitro*-3′ : 4′-*methylenedioxystilbene* from 2 : 4-dinitrotoluene (9 g.) and piperonal

(7·5 g.). Yield, 12 g. Orange-red, squat crystals, m. p. 178—180° (Found: C, 56·9; H, 3·3. $C_{15}H_{10}O_6N_2$ requires C, 57·3; H, 3·2%). 2 : 4 : 6-*Trinitro-4'-methoxystilbene*, from 2 : 4 : 6-trinitrotoluene (11 g.) and anisaldehyde (7 g.). Yield, 9·3 g. Brown needles, m. p. 167—168° (Found: C, 51·8; H, 3·3. $C_{15}H_{11}O_7N_3$ requires C, 52·2; H, 3·2%). 2 : 4-*Dinitro-4'-dimethylaminostilbene*, from 2 : 4-dinitrotoluene (9 g.) and *p*-dimethylaminobenzaldehyde (7 g.). Yield, 11 g. Small, black, lustrous plates, m. p. 181° (Found: N, 12·8. $C_{16}H_{15}O_4N_3$ requires N, 12·8%). The base forms a *chloroplatinate*, yellowish-brown needles, m. p. 211° [Found: Pt, 18·8. $(C_{16}H_{15}O_4N_3)_2,H_2PtCl_6$ requires Pt, 18·9%].

Preparation of Azoxy-compounds. General Method and Remarks.—The nitro-compound is dissolved in the smallest possible quantity of boiling alcohol, sufficient ketol for the reduction of somewhat less than the whole of the nitro-compound is added, and then a few drops of 6% alcoholic sodium methoxide or ethoxide. The solution goes dark, but soon begins to clear and a yellow or an orange precipitate settles out. After cooling a little, this is collected, dried, and recrystallised from xylene. The azoxy-compounds so obtained are, in general, yellow or bronze-yellow, and are very slightly soluble in the common solvents, slightly soluble in boiling xylene, and more soluble in boiling pyridine. If too much reducing agent be added, the reduction products are sometimes red, probably due to the formation of traces of azo-compounds.

The constitutions of the *p*-azoxystilbenes follow from the analytical figures and the molecular-weight determinations, and from their analogy to the other compounds described in this paper. That it is the *p*-nitro-group which is reduced in stilbenes containing more than one nitro-group may be safely assumed, since it has been proved already that other alkaline reducing agents, *e.g.*, ammonium sulphide, attack the *p*-nitro-group first (Thiele and Escales, *Ber.*, 1901, **34**, 2846). The insolubility of the *p*-azoxystilbenes which have been prepared so far by this method has rendered the examination of further reduction products impossible.

p-*Azoxybenzylideneaniline*, $(C_6H_5\cdot N{:}CH\cdot C_6H_4)_2N_2O$. *p*-Nitrobenzylideneaniline (8 g.) and benzoin (8 g.) gave an almost immediate separation of yellow flakes which, recrystallised from xylene, sintered at 185° and melted and decomposed at 226°. Yield, 5 g. (Found: C, 77·2; H, 5·2; N, 13·8. Calc.: C, 77·2; H, 4·95; N, 13·8%). The compound was completely identified by treating it with 27% nitric acid; *p*-azoxybenzaldehyde, m. p. 190°, and aniline were obtained (compare Alway, *Amer. Chem. J.*, 1902, **28**, 43). The *p*-azoxybenzaldehyde recondensed with aniline to give *p*-azoxybenzylideneaniline which, when mixed with the product

obtained by using benzoin as reducing agent, did not alter its melting point.

p-*Azoxybenzylidene*-p-*toluidine*, $(C_7H_7N{:}CH{\cdot}C_6H_4)_2N_2O$. *p*-Nitrobenzylidene-*p*-toluidine (2·5 g.) and benzoin (2·1 g.) gave an immediate separation of yellow flakes, which were recrystallised from boiling xylene. M.p. 217° (decomp.; sintering at 189—190°). Yield, 1·7 g. (Found: C, 77·9; H, 5·9; N, 12·5. Calc.: C, 77·7; H, 5·55; N, 12·9%).

p-*Azoxybenzylidene*-p-*aminoacetophenone*,

$(CH_3{\cdot}CO{\cdot}C_6H_4{\cdot}N{:}CH{\cdot}C_6H_4)_2N_2O$.

p-Nitrobenzylidene-*p*-aminoacetophenone (2·7 g.) and benzoin (2·1 g.) gave an immediate separation of yellow flakes. Recrystallised from xylene, the substance sintered at 187° and melted and decomposed at 217°. Yield, 1·8 g. (Found: C, 73·4; H, 5·15; N, 11·3; *M*, cryoscopic in 2 : 4-dinitrotoluene, 486. $C_{30}H_{24}O_3N_4$ requires C, 73·8; H, 4·9; N, 11·6%; *M*, 488).

p-*Azoxybenzonitrile*.—*p*-Nitrobenzonitrile was prepared by Sandmeyer's method (*Ber.*, 1885, **18**, 1492), but was isolated, not by sublimation, but by extracting the cuprocyanide reaction mixture several times with much boiling water; it was deposited in flakes on cooling and recrystallised from alcohol (yield, 8·2 g. from 13·8 g. of *p*-nitroaniline).

p-Nitrobenzonitrile (6 g.) and benzoin (8·5 g.) were dissolved in 100 c.c. of alcohol, and a few drops of 6% alcoholic sodium ethoxide added. p-*Azoxybenzonitrile* soon began to separate and after cooling it was collected and recrystallised from boiling toluene (yield, 5 g.); m. p. 221° (Found: C, 67·9; H, 3·5; N, 22·5; *M*, cryoscopic in 2 : 4-dinitrotoluene, 247. $C_{14}H_8ON_4$ requires C, 67·7; H, 3·2; N, 22·5%; *M*, 248).

Esters of p-*azoxycinnamic acid*. Ethyl *p*-nitrocinnamate (3 g.) and benzoin (3 g.) gave ethyl *p*-azoxycinnamate (2·1 g.), which crystallised from xylene in yellow, flocculent needles, m. p. 240°, sintering at 140° (Found: C, 67·1; H, 5·5; N, 7·1. Calc.: C, 67·1; H, 5·5; N, 7·2%).

Methyl *p*-nitrocinnamate (2 g.) and benzoin (2 g.) gave 1·4 g. of methyl *p*-azoxycinnamate, which crystallised from xylene in yellow, flocculent needles, m. p. 246°, sintering at 220° (Found: C, 65·8; H, 4·8; N, 7·35. Calc.: C, 65·6; H, 4·9; N, 7·6%).

p-Azoxycinnamic acid was obtained, by hydrolysis of either of the esters, as a yellow, amorphous solid insoluble in the common organic solvents but soluble in alkali; it decomposed at a high temperature (Found: C, 64·2; H, 4·3; N, 7·8. Calc.: C, 63·9; H, 4·1; N, 8·2%).

p-*Azoxystilbene*, $(C_6H_5{\cdot}CH{:}CH{\cdot}C_6H_4)_2N_2O$. 4-Nitrostilbene (1·7 g.)

and benzoin (1·6 g.), treated according to the general method, gave a green solution which in a short time turned yellow and deposited a yellow, flocculent precipitate. This, after recrystallisation from xylene, sintered at 259° and melted and decomposed at 271—272° (Found: C, 83·2; H, 5·6; N, 6·9; *M*, 396. $C_{28}H_{22}ON_2$ requires C, 83·5; H, 5·5; N, 6·9%; *M*, 402).

p-*Azoxy*-2-*nitrostilbene*. Reduction of 2 : 4-dinitrostilbene (Bishop and Brady, J., 1922, **121**, 2367) (2·6 g.) with benzoin (2·1 g.), anisoin (2·6 g.), or furoin (1·9 g.) gave 1·8 g., 1·75 g., or 1·8 g., respectively, of the p-*azoxy*-compound, which crystallised from xylene in orange plates, m. p. 208—210° (Found: C, 68·2; H, 4·2; N, 11·4; *M*, 487. $C_{28}H_{20}O_5N_4$ requires C, 68·3; H, 4·1; N, 11·3%; *M*, 492). Anisil, m. p. 133°, and furil, m. p. 162°, were obtained from their respective mother-liquors.

p-*Azoxy*-2 : 3′-*dinitrostilbene*. 2 : 4 : 3′-Trinitrostilbene (1·6 g.) and benzoin (1·1 g.) gave 0·75 g. of the reduction compound, which crystallised from xylene in yellow flakes, m. p. 212° (Found: C, 58·1; H, 3·4; N, 14·4. $C_{28}H_{18}O_9N_6$ requires C, 57·7; H, 3·1; N, 14·4%).

p-*Azoxy*-2 : 4′-*dinitrostilbene*. Only traces of this reduction compound could be isolated, since it was difficult to find a suitable solvent for the nitrostilbene.

p-*Azoxy*-2 : 6-*dinitrostilbene*. 2 : 4 : 6-Trinitrostilbene (Bishop and Brady, *loc. cit.*) (3·2 g.) and benzoin (2·1 g.) gave on standing over-night a small yield of a solid which, recrystallised from glacial acetic acid, had m. p. 270° (Found: N, 14·6. $C_{28}H_{18}O_9N_6$ requires N, 14·4%).

p-*Azoxy*-2-*nitro*-4′-*methoxystilbene*. 2 : 4-Dinitro-4′-methoxystilbene (3·1 g.) and benzoin (2·1 g.) gave 2·2 g. of the *azoxy*-compound, which is only slightly soluble in boiling xylene and is an orange-red, microcrystalline powder, m. p. 208° (Found: C, 65·8, 64·75, 64·75; H, 4·7, 4·5, 4·6; N, 10·0; *M*, 512. $C_{30}H_{24}O_7N_4$ requires C, 65·2; H, 4·3; N, 10·1%; *M*, 552).

p-*Azoxy*-2-*nitro*-3′ : 4′-*methylenedioxystilbene*. 2 : 4-Dinitro-3′ : 4′-methylenedioxystilbene (2·8 g.) and benzoin (2·1 g.) gave 1·7 g. of the p-*azoxy*-compound which, recrystallised from xylene, formed a red, microcrystalline solid, m. p. 230° (Found: C, 62·1; H, 4·0; N, 9·4; *M*, 586. $C_{30}H_{20}O_9N_4$ requires C, 62·0; H, 3·5; N, 9·6%; *M*, 580).

p-*Azoxy*-2 : 6-*dinitro*-4′-*methoxystilbene*. 2 : 4 : 6-Trinitro-4′-methoxystilbene (2·8 g.) and benzoin (2·1 g.) gave 1·25 g. of the p-*azoxy*-compound, which forms bronze plates from xylene. It changes colour at 252° and melts with decomposition at 297° (Found: C, 55·6; H, 3·6; N, 13·2. $C_{30}H_{22}O_{11}N_6$ requires C, 55·9; H, 3·4; N, 13·06%).

p-*Azoxy*-2-*nitro*-4′-*dimethylaminostilbene*. 2 : 4-Dinitro-4′-dimethylaminostilbene (1·5 g.) and benzoin (1 g.) gave black, flaky crystals of the p-*azoxy*-compound which were washed with hot alcohol. The compound is so slightly soluble in boiling xylene that it cannot be recrystallised from that solvent. The substance without further purification remained unchanged at 305° (Found: N, 14·3. $C_{32}H_{30}O_5N_6$ requires N, 14·5%). The compound is soluble in hot concentrated hydrochloric acid, but the hydrochloride is readily hydrolysed on addition of water. Two attempts to prepare a chloroplatinate failed owing to the almost colloidal nature of the hydrochloric acid solution.

The mother-liquors from each of the above reductions in which benzoin was used yielded benzil, m. p. 95°, on standing or when poured into water and the needles so obtained were recrystallised from alcohol. The compound was identified by its characteristic reaction with alcoholic potash and by its oxidation to benzoic acid, m. p. 122°, by means of alkaline permanganate.

The investigation is being continued with a view to establishing the generality of this method of reducing nitro- to azoxy-groups and determining its value as a method of preparing azoxy-compounds.

In concluding this part of the work, the author desires to thank Professor A. Archibald Boon for his kind interest and for providing the facilities which have rendered this research possible.

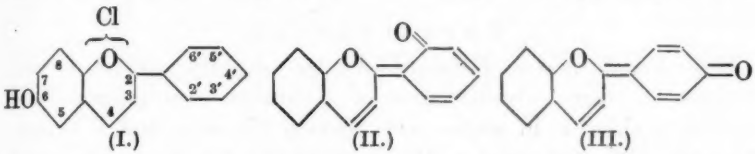
HERIOT-WATT COLLEGE, EDINBURGH. [*Received, June 20th*, 1927.]

CCLXXVI.—*A Synthesis of Pyrylium Salts of Anthocyanidin Type. Part XIII. Some Monohydroxyflavylium Salts.*

By FRANK MOUATT IRVINE and ROBERT ROBINSON.

IT was thought that a study of some of the simpler hydroxyflavylium salts might throw light on the effects produced by hydroxy-groups in different positions in the three nuclei, especially from the point of view of anhydro-base and pseudo-base formation. Solutions of 3-hydroxyflavylium chloride have been obtained by demethylation of the methyl ether (Pratt and Robinson, J., 1923, **123**, 748), but this salt showed such a strong tendency to pass into the pseudo-base that it could not be isolated in a pure condition. It dissolves in sulphuric acid to a solution that exhibits intense plum-coloured fluorescence. 6-Hydroxyflavylium chloride (I) is less readily

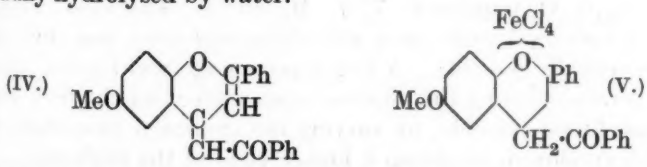
hydrolysed, but also yields a colourless pseudo-base, a quinonoid anhydro-base not being possible without the postulation of " bridge-bonds." This is merely one more example among many which



(I.) (II.) (III.)

show that aromatic structures assume a bridge-phase with the greatest reluctance. In the cases of 2′- and 4′-hydroxyflavylium salts, anhydro-bases of the types (II) and (III) are possible. Actually the anhydro-bases derived from 2′-hydroxyflavylium chloride and 2′-hydroxy-8-methoxyflavylium chloride are violet substances that could not be isolated owing to their marked tendency to pass into pseudo-bases by hydration. Thus the quinones are not formed by dehydration of pyranols, but are directly obtained from the kations of the pyrylium salts by removal of a proton under the influence of anions. The colour-base from 4′-hydroxyflavylium chloride is apparently a quinhydrone having the composition $C_{15}H_{10}O_2,C_{15}H_{12}O_3,2H_2O$; by analogy with the suggestions of Schneider and Meyer (*Ber.*, 1921, **54**, 1484) it may be named 4′-*hydroxyflavanhydrone*. The molecular weight of the anhydrous compound corresponded with this formula, and similar results were obtained in the study of 4′-*hydroxy*-8-*methoxyflavanhydrone*.

Incidentally 6-*methoxy*-4-*phenacylideneflavene* (IV) has been examined and found to yield a *hydroferrichloride* (V) which is readily hydrolysed by water.



Moreover, the carbonyl group in (IV) is inactive, so that the resemblance to the pyrones is complete, the system −O−C=C−C=O being extended to −O−C=C−C=C−C=O. Probably the phenacylideneflavenes are dipoles and anhydronium bases in the sense in which that expression was used by Armit and Robinson (J., 1925, **127**, 1607). In view of the remarkable rearrangement of the anhydro-base from 2 : 6-diphenyl-4-*o*-hydroxyphenylpyrylium chloride to phenacylideneflavene (Dilthey and Floret, *Annalen*, 1924, **440**, 95), alternative formulæ for the latter substance would appear to require consideration. However, Dilthey and Floret have excluded

possibilities based on the triphenylpyrylium skeleton on the ground that phenacylideneflavene gives a small quantity of flavone when oxidised by permanganate.

EXPERIMENTAL.

8-Methoxyflavylium Chloride.—Under slightly modified conditions, the direct condensation of *o*-vanillin, acetophenone, and hydrogen chloride in acetic acid solution (Roberts and Robinson, J., 1924, **125**, 209) gave a 70% yield of the flavylium salt, which crystallised from dilute hydrochloric acid in brown needles which blackened at 170° and melted at 190° (decomp.) (Found in material dried in a vacuum: C, 66·2; H, 5·2. $C_{16}H_{13}O_2Cl,H_2O$ requires C, 66·1; H, 5·1%). The *iodide* crystallises from dilute, colourless hydriodic acid in puce-coloured needles, m. p. 134°. All attempts to demethylate these salts were unsuccessful.

Phenyl 2-Hydroxy-5-methoxystyryl Ketone.—2-Hydroxy-5-methoxybenzaldehyde (5·1 g.; 1 mol.) and acetophenone (4 g.; 1 mol.) in ethyl alcohol (30 c.c.) were mixed with a warm solution of potassium hydroxide (13 g.; 7 mols.) in water (13 c.c.) and left in a warm place over-night. The solution was poured into water (400 c.c.), kept for an hour until the waxy precipitate (A) had solidified, and then filtered. The filtrate and washings were acidified with 50% acetic acid and the chalkone was collected and dried (yield, 4·25 g. or 50%). It crystallised from benzene or from 50% alcohol in clusters of fine, golden-yellow needles, m. p. 104° (Found: C, 75·5; H, 5·4. $C_{16}H_{14}O_3$ requires C, 75·6; H, 5·5%).

The residue (A) was thrice recrystallised from alcohol; it formed stellate clumps of short, white needles, m. p. 125° (Found: C, 77·0; H, 6·0. $C_{24}H_{22}O_4$ requires C, 77·0; H, 5·9%). The yield (2·6 g.) of this *2-hydroxy-5-methoxybenzylidenediacetophenone* was 40% of that theoretically possible. A larger percentage was formed when the temperature during the alkaline condensation was higher; but it was not found possible, by varying the molecular proportion of the alkali employed, to obtain a higher yield of the chalkone.

6-Methoxyflavylium Salts.—Phenyl 2-hydroxy-5-methoxystyryl ketone was converted into 6-methoxyflavylium chloride by means of hydrogen chloride in acetic acid solution. The reaction proceeded to completion in the cold, passing through the red ketone-hydrochloride stage. The flavylium salt partly crystallised and was partly precipitated by the addition of ether. It was collected and dried to constant weight in a vacuum (Found: C, 62·3; H, 5·5. $C_{16}H_{13}O_2Cl,2H_2O$ requires C, 62·2; H, 5·5%). The salt crystallised from 5% hydrochloric acid in dark greenish-brown, shining needles, m. p. 97°. Its yellow solution in concentrated sulphuric acid

exhibited a weak green fluorescence, but the orange-yellow alcoholic solution was non-fluorescent. The *ferrichloride* crystallised from acetic acid in glistening, brown platelets with green nuance, m. p. 203° (Found : C, 44·0; H, 3·2; Fe, 12·7. $C_{16}H_{13}O_2Cl_4Fe$ requires C, 44·1; H, 3·0; Fe, 12·9%). The *iodide* crystallised from alcohol in almost black, microscopic needles, m. p. 143°, whilst the *periodide* had m. p. 86—87°. The *perchlorate* crystallised from 60% methyl alcohol in short, dark brown needles, m. p. about 200° (decomp.).

6-*Hydroxyflavylium Salts.*—The demethylation required rather careful control. A mixture of 6-methoxyflavylium chloride dihydrate (8·8 g.), phenol (40 g.), and hydriodic acid (*d* 1·74; 150 c.c.) was heated in a glycerol-bath at 110°, until the effluent stream of carbon dioxide no longer contained methyl iodide (45 minutes). The mixture was diluted with an equal volume of water and of ether, cooled in ice, and filtered; the black crystals (6·4 g.) had a green lustre. After the ethereal layer had been separated, the remainder (about 3·6 g.) of the iodide, mixed with periodide, could be recovered by evaporating the filtrate under reduced pressure in an atmosphere of hydrogen. The demethylated product (7 g.) was dissolved in the minimum volume of hot alcohol (700 c.c.) and concentrated hydrochloric acid (200 c.c.), and freshly precipitated silver chloride (from 7 g. of silver nitrate) added. The mixture was gently boiled during 5 minutes while being stirred; it was then filtered hot, and the residue washed with hot ethyl-alcoholic hydrochloric acid. The filtrate and washings were concentrated to a small volume and cooled, and the 6-*hydroxyflavylium chloride* was collected; it crystallised from alcohol or from 15% hydrochloric acid in orange needles. The chloride was very readily hydrolysed by water, and the pseudo-base was also formed when sodium acetate was added. The *ferrichloride* crystallised from glacial acetic acid in short, reddish-brown needles, m. p. 198° (Found : C, 43·1; H, 2·7; Fe, 13·2. $C_{15}H_{11}O_2Cl_4Fe$ requires C, 42·8; H, 2·6; Fe, 13·3%). The *chloroaurate* formed golden-brown needles which on heating turned grey at 180° but did not melt. 6-Hydroxyflavylium salts give, in concentrated sulphuric acid, orange solutions with a green fluorescence.

4′-*Hydroxyflavylium Salts.*—*p*-Methoxyacetophenone was condensed with salicylaldehyde to form *p*-methoxyphenyl *o*-hydroxystyryl ketone as described by Kostanecki and Zwayer (*Ber.*, 1908, **41**, 1337) and the yield of the pure, recrystallised product was 81%. The chalkone (13·8 g.) was dissolved in a mixture of glacial acetic acid (50 c.c.) and concentrated hydrochloric acid (25 c.c.) by saturating this with hydrogen chloride, and the solution after an hour was gently warmed for 15 minutes and poured into water. An

excess of potassium iodide was added to the filtered solution of the flavylium chloride and an orange precipitate of the anhydrous *4′-methoxyflavylium iodide* was formed (yield, 89%). This salt (17·2 g.) was gently refluxed for ½ hour with hydriodic acid (300 c.c.; *d* 1·74) and phenol (70 g.) in an atmosphere of carbon dioxide. On cooling, crystals (9·4 g.) separated which were pure enough for the next operation; for analysis, they were recrystallised from methyl alcohol, being thus obtained in dark purple prisms (Found: C, 29·8; H, 2·0; I, 62·7. $C_{15}H_{11}O_2I_3$ requires C, 29·8; H, 1·8; I, 63·1%). *4′-Hydroxyflavylium periodide* melts at 208—209° and decomposes suddenly at 285°; when pressed on glass, it has a beetle-green lustre. Freshly precipitated silver chloride (from 2·85 g. of silver nitrate) was added to a solution of the periodide (2 g.) in a hot mixture of methyl alcohol (125 c.c.) and 7·5% hydrochloric acid (100 c.c.), and the whole was boiled for 15 minutes and filtered. The filtrate and washings were concentrated and, on cooling, red needles separated (yield, 80%). This product was crystallised several times from dilute hydrochloric acid in order to remove traces of inorganic impurities which were tenaciously held. The clusters of fine, orange-red needles, after drying over sulphuric acid and potassium hydroxide, darkened at 135° and melted at 142° (decomp.) (Found: C, 61·2, 61·0; H, 5·1, 5·3. $C_{15}H_{11}O_2Cl,2H_2O$ requires C, 61·1; H, 5·1%). This salt dissolves in water or alcohol to an orange solution which becomes yellow on the addition of a drop of dilute hydrochloric acid or red with weakly alkaline reagents. The orange solution in concentrated sulphuric acid exhibits a green fluorescence. The *chloroaurate* crystallises in golden-orange needles, m. p. 177°.

4′-Hydroxyflavanhydrone.—A solution of 4′-hydroxyflavylium chloride in water was covered with benzene, and excess of sodium acetate added; on shaking, a portion of the violet-red substance was dissolved by the benzene, which was separated, dried with potassium carbonate, and filtered. The dark violet solid which remained on removal of the solvent could not be crystallised (Found: C, 72·0; H, 5·7; loss on heating at 110°/15 mm., 7·4. $C_{30}H_{22}O_5,2H_2O$ requires C, 72·3; H, 5·2; H_2O, 7·2%. Found in dried material: C, 77·6; H, 4·9; *M*, by micro-Rast, 472. $C_{30}H_{22}O_5$ requires C, 77·9; H, 4·8%; *M*, 462). On further heating, the deep red substance gradually sintered and was completely molten at 200°. The red solution in pyridine became colourless in a few seconds, probably as the result of the formation of the benzopyran ether (compare Dilthey, *J. pr. Chem.*, 1917, **95**, 113, 117). This flavanhydrone showed no tendency to combine with methyl iodide.

4′-Hydroxy-8-methoxyflavylium Salts.—The method of Nencki and

Stoeber (*Ber.*, 1897, **30**, 1769) for the preparation of *p*-hydroxyacetophenone only gives a 10% yield and the product is difficult to purify. The following modification is much more satisfactory: Powdered anhydrous ferric chloride (81 g.) was added to a solution of phenol (63 g.) in carbon disulphide (48 c.c.), and acetyl chloride (95 c.c.) was then introduced drop by drop with shaking. When the addition was complete, the mixture was shaken during 5 minutes and the carbon disulphide and acetyl chloride were then carefully removed by distillation. The residue was decomposed by water and rendered alkaline with sodium hydroxide, the solution decanted from the ferric hydroxide, which was washed by decantation, and the crude *p*-hydroxyacetophenone precipitated by acidification. After crystallisation from water, 30 g. (yield, 33%), m. p. 110°, were obtained. p-*Acetoxyacetophenone*, m. p. 54°, crystallises from alcohol and was obtained in 80% yield on agitating an aqueous solution of sodium *p*-acetylphenoxide (1 mol.) with acetic anhydride (1 mol.).

A stream of hydrogen chloride was passed through a solution of *o*-vanillin (1·1 g.) and *p*-hydroxyacetophenone (1 g.) in formic acid (10 c.c.) for 1 hour, and the mixture kept until next day. The orange solid precipitated on the addition of ether crystallised from 10% hydrochloric acid (60 c.c.) in brick-red needles (1·6 g.) (Found in material dried in a vacuum: C, 62·3; H, 4·8. $C_{16}H_{13}O_5Cl,H_2O$ requires C, 62·6; H, 4·9%). This salt darkens at 170° and melts at 190° (decomp.); it dissolves in water to a yellow solution exhibiting a weak green fluorescence. The *ferrichloride* crystallised from acetic acid in reddish-brown needles, m. p. 217°, and the *periodide* crystallised in chocolate-coloured needles, m. p. 170—173° (decomp.), after darkening at 140°. The ruby benzene solution of the anhydro-base, prepared in the usual manner, was dried with potassium carbonate and, on removal of the solvent from the filtered solution, a deep purplish-red solid residue was obtained, which was dried in a vacuum (Found: C, 73·7; H, 5·4. $C_{32}H_{26}O_7$ requires C, 73·6; H, 5·0%). The molecular weight could not be determined by Rast's method and no solvent was found to be suitable for recrystallisation; in several solvents, for example, acetone and nitrobenzene, it gave bottle-green solutions. On heating, this 4′-*hydroxy*-8-*methoxyflavanhydrone* gradually sintered and decomposed at 206°.

2′-*Hydroxyflavylium Ferrichloride.*—The condensation of salicylaldehyde with *o*-hydroxyacetophenone (Fries and Pfaffendorf, *Ber.*, 1910, **43**, 215), under conditions similar to those mentioned below, gave a bright scarlet, very sparingly soluble solid, which is not a flavylium salt and is apparently of complex constitution.

The hydroxyl group in the ketonic component was therefore protected by acetylation (compare Friedländer and Neudorfer, *Ber.*, 1897, **30**, 1080; Lesser and Gad, *Ber.*, 1926, **59**, 233). A solution of *o*-acetoxyacetophenone (0·9 g.) and salicylaldehyde (0·6 g.) in formic acid (6 c.c.) was saturated with hydrogen chloride during 3 hours, and next day the red solid, which was precipitated on the addition of ether, was collected and extracted with 17% hydrochloric acid (60 c.c.), leaving a considerable residue. A *ferrichloride* prepared from the filtered solution crystallised from acetic acid in tufts of brown needles, m. p. 125° (Found: C, 42·6; H, 2·7; Fe, 13·3. $C_{15}H_{11}O_2Cl_4Fe$ requires C, 42·8; H, 2·6; Fe, 13·3%). The orange solution in sulphuric acid exhibits a weak green fluorescence. The solution of the ferrichloride in dilute hydrochloric acid gave, with a large excess of sodium carbonate solution, quickly added, a transient purple colour. The colourless filtrate from the ferric hydroxide apparently contained pseudo-base in solution, for on acidification it turned bright yellow, and then, on addition of a large excess of sodium carbonate, the purple colour flashed out, but the solution became almost instantaneously colourless. The purple colour was formed only if the sodium carbonate was added quickly and in large excess.

2′-Hydroxy-8-methoxyflavylium Salts.—Several attempts to prepare 2′-hydroxy-8-methoxyflavylium chloride by condensing *o*-vanillin (1 mol.) and *o*-acetoxyacetophenone (1 mol.) in anhydrous formic acid with hydrogen chloride failed during the recrystallisation from hot dilute hydrochloric acid (in order to remove the acetyl group in the 2′-position), probably because some complex substance, not a pyrylium salt, was formed in this case also. The use of unacetylated *o*-hydroxyacetophenone led to better results in this instance. A solution of *o*-hydroxyacetophenone (1·4 g.) and *o*-vanillin (1·5 g.) in formic acid (6 c.c.) was saturated with hydrogen chloride for 1·5 hours and on the following day ether precipitated a reddish-brown solid, which crystallised from methyl alcohol in long, red needles; these darkened above 100° and had m. p. 188° (decomp.) (Found: C, 66·3; H, 4·7. $C_{16}H_{13}O_5Cl$ requires C, 66·5; H, 4·5%). This salt dissolved in sulphuric acid to an orange solution exhibiting a weak green fluorescence. When water was added to the solid chloride or to its solution in alcohol, the pseudo-base was obtained; this dissolved with difficulty in dilute hydrochloric acid. Sodium acetate, added in excess to an acid solution of this salt, produced the violet colour-base, which could be extracted by benzene; the colour of the violet solution, however, soon faded. Again, when the colour-base was quickly separated, the filtrate was always found to contain pseudo-base. This remarkable ease of

hydration of the anhydro-base derived from a flavenol has not previously been observed in the absence of a substituent in position 3.

6-*Methoxyphenacylideneflavene* (V).—Following the details given by Feuerstein and Kostanecki (*Ber.*, 1898, **31**, 710) in the case of the parent substance, 2-hydroxy-5-methoxybenzylidenediacetophenone (7·5 g.) was converted into acetophenone (1·1 g.), *phenyl* β-2-*hydroxy*-5-*methoxyphenylethyl ketone* (2·3 g.), and 6-*methoxyphenacylideneflavene* (3·8 g.). The last compound crystallised from alcohol or benzene in yellow, feathery clusters of fine needles, m. p. 146° (Found: C, 80·7, 80·8; H, 5·0, 5·0; MeO, 8·8. $C_{24}H_{18}O_3$ requires C, 81·4; H, 5·1; MeO, 8·8%). In the micro-Zeisel determination, the mixture required to be heated almost twice as long as usual. The solution in cold sulphuric acid was yellowish-orange and non-fluorescent, and on warming a transitory purple colour appeared, succeeded by a ruby one.

Pure 6-methoxyphenacylideneflavene (1·8 g.) was suspended in acetic acid (10 c.c.), and a stream of dry hydrogen chloride passed during 3 minutes; on shaking, all the solid dissolved to a red solution. The addition of a solution of anhydrous ferric chloride (0·8 g.) in glacial acetic acid (5 c.c.) produced an immediate red precipitate, which soon became brownish-orange and crystalline. After keeping for an hour, the flask being stoppered, the solid was collected and dried over sulphuric acid and potassium hydroxide (yield, 2·54 g. or 92%) (Found: C, 52·0; H, 3·5; Fe, 10·0; MeO, 5·8. $C_{24}H_{19}O_3Cl_4Fe$ requires C, 52·1; H, 3·4; Fe, 10·1; MeO, 5·6%).

6-*Methoxy*-4-*phenacylflavylium ferrichloride* forms microscopic, elongated prisms which melt, with blackening, at 170° (on slow heating). It is sparingly soluble in water to an orange solution which slowly deposits 6-methoxyphenacylideneflavene; this hydrolysis is, however, very rapid in presence of alcohol. The ferrichloride gives an orange, non-fluorescent solution in sulphuric acid.

6-Methoxyphenacylideneflavene (1 mol.) did not react when refluxed in benzene solution for ¼ hour with magnesium phenyl bromide (1 mol. prepared in ether).

The *phenyl* β-2-*hydroxy*-5-*methoxyphenylethyl ketone* was a brown syrup with a strong green reflex. Although its hydroxyl group could not be acetylated or benzoylated, its carbonyl group was reactive, and the *semicarbazone* and p-*nitrophenylhydrazone* were readily prepared. The former crystallised from alcohol in white, elongated prisms, m. p. 184° (Found: C, 65·1; H, 6·5; N, 13·5. $C_{17}H_{19}O_3N_3$ requires C, 65·2; H, 6·1; N, 13·4%), and the latter separated from alcohol in microscopic, orange needles, m. p. 163—

165°. The ketone itself could not be crystallised. The same hydrochalkone was obtained, also as a syrup, and identified as the semicarbazone, m. p. 184° (alone or mixed), by the catalytic reduction of phenyl 2-hydroxy-5-methoxystyryl ketone with a palladium catalyst.

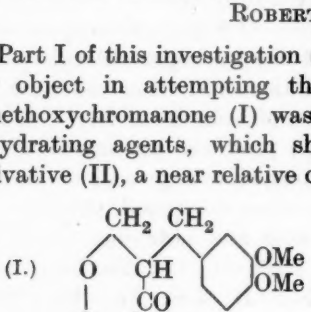
THE UNIVERSITY, MANCHESTER. [*Received, June 28th*, 1927.]

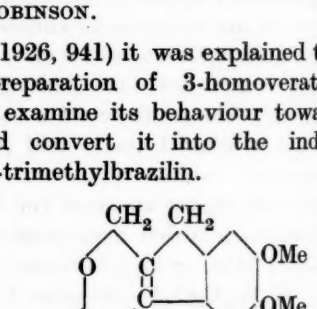
CCLXXVII.—*Experiments on the Synthesis of Brazilin and Hæmatoxylin and their Derivatives. Part II. A Synthesis of Deoxytrimethylbrazilone and of* iso*Brazilein Ferrichloride Trimethyl Ether.*

By WILLIAM HENRY PERKIN, jun., JNANENDRA NATH RÂY, and ROBERT ROBINSON.

IN Part I of this investigation (J., 1926, 941) it was explained that our object in attempting the preparation of 3-homoveratryl-7-methoxychromanone (I) was to examine its behaviour towards dehydrating agents, which should convert it into the indene derivative (II), a near relative of *O*-trimethylbrazilin.

(I.)



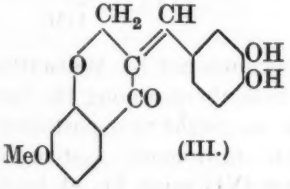


(II.)

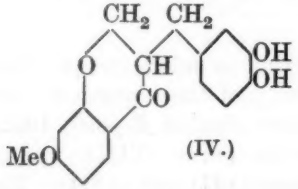
Considerable progress in this direction has since been made and we had hoped to be able to defer publication until our experiments on the final stages of the synthesis of trimethylbrazilin were completed; an interim report has, however, become necessary as the result of a communication received on June 7th from Professor P. Pfeiffer and we therefore submit at once an account of the stage already reached in our work. Professor Pfeiffer's letter mentions results similar in many respects to those which we have obtained and in view of this duplication of research we wish to direct attention to the clear statement of our position which we thought it wise to make at the time of publication of Part I of this series (*loc. cit.*, p. 942) and which it is unnecessary to repeat. The reduction of veratrylidene-7-methoxychromanone by means of hydrogen in presence of palladium yielded (*loc. cit.*, p. 946) 3-homoveratryl-7-methoxychroman, m. p. 96°, instead of the expected ketone (I), which, however, Pfeiffer and Emmer (*Ber.*, 1920, **53**, 945) claimed

to have obtained when they employed platinum as the catalyst. The ketone was stated to melt at 89° and in Part I we expressed some doubt in regard to the accuracy of the interpretation of their results. Since, however, we had not repeated these experiments, our remarks were guarded and summarised in the statement (p. 947): "We do not go so far as to assert that the products of hydrogenation of veratrylidenemethoxychromanone in presence of platinum and of palladium are identical, although we think it probable that this will prove to be the case." The suggestion so expressed was, however, not correct, as the experiments mentioned below indicate, and Professor Pfeiffer informs us that he has re-examined his substance and proved that it is a ketone by the preparation of its oxime. Although we were unable to accomplish satisfactorily the reduction of veratrylidenemethoxychromanone to a related saturated ketone, the formation of the saturated ketone (IV) from 3 : 4-dihydroxybenzylidene-7-methoxychromanone (III) proceeds smoothly under these conditions.

This substance (III) was obtained by the condensation of protocatechualdehyde with 7-methoxychromanone (a new and improved method for the preparation of which is described on p. 2097) in acetic acid solution by means of hydrogen chloride. On methylation in the usual manner, (IV) yields the ketone (I), which has m. p. 92°, and the whole of the substance which we have used in this investigation was prepared in this way. Subsequently the same compound was isolated in poor yield from the products of the partial hydrogenation of veratrylidenemethoxychromanone in presence of palladium.



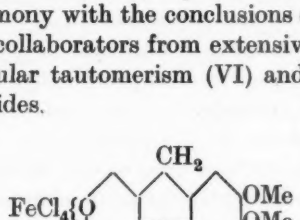
(III.)



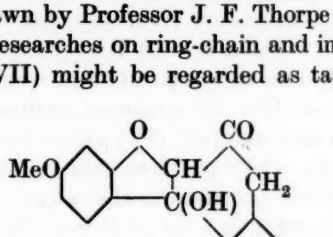
(IV.)

On treatment with phosphoric anhydride in boiling benzene the dehydration of (I) to (II) was effected, and the first indication of its structure and of the fact that it contains the brazilin skeleton was provided by the oxidation of the crude substance to *iso*brazilein ferrichloride trimethyl ether (V) (Engels, Perkin, and Robinson, J., 1908, **93**, 1121; Crabtree and Robinson, J., 1918, **113**, 859), a process effected by means of ferric chloride in acetic acid solution. The salt was identified by comparison with an authentic specimen prepared from brazilein. Later, the compound (II) was obtained from (I) in a pure condition by the dehydrating action of phosphoric anhydride and identified by direct comparison with deoxytrimethyl-

brazilone, $C_{19}H_{18}O_4$, a substance obtained by the reduction of trimethylbrazilone, $C_{19}H_{18}O_6$, with phenylhydrazine (Gilbody and Perkin, J., 1902, **81**, 1046). Deoxytrimethylbrazilone, prepared from brazilin, was also found to yield the *iso*brazilein derivative in the manner described above. Professor Pfeiffer's letter directs attention to the possibility that his dehydration product of the ketone (I) may be deoxytrimethylbrazilone and that the pyrylium salt which it yields on oxidation with ferric chloride may be *iso*-brazilein ferrichloride trimethyl ether. The synthetical proof that deoxytrimethylbrazilone has the constitution (II) and contains the brazilin skeleton necessitates a view of the nature of trimethyl-brazilone differing somewhat from that expressed in the formula (VI) (Perkin and Robinson, J., 1908, **93**, 948). It was then suggested that the oxidation of trimethylbrazilin with chromic acid leads to the disruption of the bond common to the chroman and hydrindene nuclei and to the production of a diketone (VII) which passes into (VI) by an intramolecular aldol condensation. In harmony with the conclusions drawn by Professor J. F. Thorpe and his collaborators from extensive researches on ring-chain and intra-annular tautomerism (VI) and (VII) might be regarded as tautomerides.

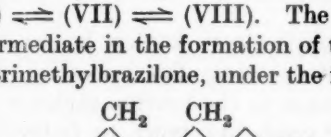


(V.)

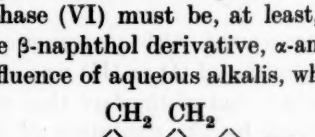


(VI.)

Bearing in mind the phenomena encountered by Willstätter in his study of the *o*-quinones and by Schönberg among the benzils (compare *Annual Reports*, 1922, 109), we might also postulate the peroxidic phase (VIII), the complete tautomeric system being (VI) $\rightleftharpoons$ (VII) $\rightleftharpoons$ (VIII). The phase (VI) must be, at least, an intermediate in the formation of the β-naphthol derivative, α-anhydrotrimethylbrazilone, under the influence of aqueous alkalis, whilst



(VII.)



(VIII.)

VIII) offers an explanation of the remarkable behaviour with phenylhydrazine. Nevertheless, (VI) and (VIII) can only be

related through (VII) and the last seems to be the most satisfactory single expression of the whole character of trimethylbrazilone which it is possible to select. In this phase, some coherence of the carbonyl groups may be manifested as the result of the dipolar character of these groups.

Further evidence bearing on this aspect of the chemistry of brazilin will, it is hoped, be discussed in a future communication and it is proposed to extend the synthetical work indicated above to the analogous hæmatoxylin derivatives. Naturally we are also engaged in attempts to convert deoxytrimethylbrazilone into trimethylbrazilin.

Experimental.

7-Methoxychromanone.—The following method of preparation of this substance is much more convenient than any of those hitherto described. A solution of β-*m*-methoxyphenoxypropionic acid (14 g.) in 80% sulphuric acid (100 c.c.) was heated to 60° during an hour, then at 60—80° for an hour, and finally at 80—90° for a third hour. The ketone was isolated by means of ether in the usual manner from the diluted mixture and freed from acids. The crude product crystallised when dry and weighed 7—8 g. (yield, about 60%). Several new substances which have been prepared in the course of our work may be mentioned here. *Ethyl* β-m-*methoxyphenoxypropionate*, $MeO{\cdot}C_6H_4{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2Et$, obtained by esterification of the acid with boiling ethyl-alcoholic sulphuric acid, crystallises from aqueous alcohol in plates, m. p. 45° (Found: C, 63·8; H, 7·3. $C_{12}H_{16}O_4$ requires C, 64·3; H, 7·1%). This ester could not be condensed with veratraldehyde. *Veratrylidene-7-methoxychromanone dibromide*, prepared in cold carbon tetrachloride solution, has m. p. 137—138° (Found: C, 46·2; H, 3·6. $C_{19}H_{18}O_5Br_2$ requires C, 46·8; H, 3·7%) and yields veratrylidenemethoxychromanone on treatment with zinc dust and acetic acid.

Veratrylidenemethoxychromanone yields an *oxamino-oxime* when treated with hydroxylamine hydrochloride (3 mols.) and sodium acetate in boiling alcoholic solution. The colourless substance crystallises from alcohol in prismatic needles (Found: C, 61·0; H, 5·8; N, 7·0. $C_{19}H_{22}O_6N_2$ requires C, 61·0; H, 5·9; N, 7·5%).

3-(3′ : 4′-Dihydroxybenzylidene)-7-methoxychromanone (III).—An ice-cold solution of 7-methoxychromanone (5 g.) and protocatechualdehyde (5 g.) in acetic acid (30 c.c.) was saturated with hydrogen chloride and set aside. Next day, the garnet crystals which had separated were collected and decomposed by trituration with water at 0°. The substance crystallised from aqueous alcohol (charcoal) in brownish-yellow, microscopic needles, m. p. 212° (Found: C, 68·5; H, 4·8. $C_{17}H_{14}O_5$ requires C, 68·4; H, 4·7%).

The alcoholic solution develops a green coloration on the addition of ferric chloride. Aqueous alkaline solutions are deep crimson to blood-red according to the concentration. Methylation by means of methyl sulphate and sodium hydroxide yields veratrylidenemethoxychromanone, m. p. 141°.

3-(3′ : 4′-*Dihydroxybenzyl*)-7-*methoxychromanone* (IV).—A solution of dihydroxybenzylidenemethoxychromanone (1·5 g.) in alcohol (100 c.c.) to which palladous chloride (15 c.c. of 0·5% aqueous solution) had been added was stirred with hydrogen; 60 c.c. of the gas were absorbed at 15° in 28 minutes. The nearly colourless liquid was filtered and concentrated; the reduction product, then precipitated on dilution with water, crystallised from aqueous alcohol (about 20%) in rectangular plates, m. p. 138° (Found: C, 68·0; H, 5·7. $C_{17}H_{16}O_5$ requires C, 68·0; H, 5·3%). Ferric chloride added to an alcoholic solution of this substance produces a green coloration changing to crimson on keeping. The cherry-red solution in sulphuric acid soon acquires a yellowish-green fluorescence and on addition of water a fluorescent orange solution is obtained. The action of hydrogen chloride on this ketone in glacial acetic acid solution yielded, together with other products, a crystalline *substance*, m. p. 139° (mixed, 118—124°), the investigation of which is not yet complete.

3-*Homoveratryl*-7-*methoxychromanone* (I).—(A) The dihydric phenol described in the last section was methylated in methyl-alcoholic solution by means of methyl sulphate and potassium hydroxide in the usual manner; the product crystallised from aqueous alcohol and then from aqueous acetone in glistening, rectangular plates, m. p. 92° (Found: C, 70·1; H, 6·3. Calc. for $C_{19}H_{20}O_5$: C, 69·6; H, 6·1%). The substance is insoluble in aqueous alkalis and gives no coloration with ferric chloride in alcoholic solution.

(B) When veratrylidenemethoxychromanone was reduced in acetic acid solution by means of the calculated volume of hydrogen in presence of palladium the greater part of the unsaturated ketone was recovered unchanged, whilst an unlimited reduction gave homoveratrylmethoxychroman, m. p. 96°, as previously described (*loc. cit.*). Under the following conditions, however, the dihydro-derivative could be isolated, although in poor yield. A solution of veratrylidenemethoxychromanone (1·4 g.) in pure acetic acid (100 c.c.) to which palladous chloride (20 c.c. of 0·5% solution) had been added was agitated with hydrogen at 18°; 50 c.c. were absorbed in 12 minutes, and a further 50 c.c. in 50 minutes, after which absorption of a third equal volume occurred at 40—45°. The filtered solution was concentrated under diminished pressure

to 35 c.c., and water (10 c.c.) added, causing the precipitation of unchanged material, which was crystallised from alcohol (0·7 g., m. p. 141°). The acetic acid and alcoholic filtrates were diluted with water and the precipitated material was fractionally crystallised from aqueous alcohol and aqueous acetone. About 0·1 g. of a substance crystallising in glistening, rectangular plates, m. p. 92°, was isolated. The m. p. of a mixture with the ketone prepared as described under (A) was 92°, whilst a mixture with homoveratrylmethoxychroman, m. p. 96°, melted at 71—86°. A minute amount of the chroman derivative, m. p. 96°, was isolated from the mother-liquors.

Deoxytrimethylbrazilone (II).—There are indications that 3-homoveratrylmethoxychromanone may be dehydrated by means of a variety of condensing agents, *e.g.*, zinc chloride, stannic chloride, phosphoryl chloride, etc., in that the products are partly oxidised in acid solution to *iso*brazilein salts, the fluorescence of which is so characteristic. Phosphoric anhydride (30 g.) was added to a solution of the ketone (3·5 g.) in benzene (150 c.c.), and the solution gently boiled for 10 minutes. The dark mass was decomposed by the addition of ice, the mixture was heated and agitated, the benzene layer, separated from the strongly fluorescent aqueous solution, was washed with water and aqueous sodium hydroxide, dried with potassium carbonate (charcoal), and filtered, and the solvent was removed in a vacuum. The residue (R) was dissolved in alcohol, and the solution concentrated; the substance which separated on keeping crystallised from alcohol as a satiny mass of colourless sheaves of needles, m. p. 166—171°. This substance was found by direct comparison to be identical with deoxytrimethylbrazilone prepared by the method of Gilbody and Perkin (*loc. cit.*). This and also a mixture of the two specimens had m. p. 166—171°. The colour reactions and solubilities described by Gilbody and Perkin were identical in the cases of the synthetical specimen and that derived from brazilin. Some more details regarding the characteristic reactions of this substance may be given. The solution in an excess of nitric acid is intense eosin-red rather than purple (Gilbody and Perkin) and on dilution with water gives a clear red solution exhibiting very bright yellowish-green fluorescence. The more blue-toned red solution results, however, if the volume of nitric acid employed is greatly diminished, and dilution with water then gives the purple precipitate mentioned by Gilbody and Perkin. A benzene solution was treated with dilute nitric acid (1 vol., d 1·42, and 2 vols. of water); a crimson colour then appeared in both layers accompanied by intense yellowish-green fluorescence. On shaking, an orange substance separated from the benzene layer, the colour of which

faded. An acetic acid solution treated with a trace of bromine becomes intense crimson and the usual fluorescence is almost absent; on boiling, the colour changes to orange and dark green fluorescence appears. This becomes brilliant on dilution with alcohol and is of the *iso*brazilein type. Iodine, in most solvents, gives a similar reaction. Bromine, in an acetone solution containing hydrobromic acid, however, immediately oxidises the chromene to the pyrylium bromide, which separates in orange needles. The substance was recognised by conversion into the ferrichloride, identical with the product obtained by the method given below.

iso*Brazilein Ferrichloride Trimethyl Ether* (V).—A characteristic property of deoxytrimethylbrazilone is the ease with which it is oxidised in acid solution with formation of the *iso*brazilein salts and a convenient method is provided by the use of ferric chloride in acetic acid solution. The deoxytrimethylbrazilone was dissolved in warm acetic acid, the solution cooled, and anhydrous ferric chloride introduced; the ferrichloride soon separated as a crimson mass of needles that appeared orange by transmitted light. In some cases, and especially if cooling was used, a deep crimson ferrichloride separated in slender needles and the solution remained red. This was an intermediate product and, on gently warming, the solution became orange and the brownish-orange *iso*brazilein ferrichloride trimethyl ether separated at once. In this form the substance was practically pure and after one crystallisation from acetic acid was identified by careful comparison with a specimen obtained from pure tetramethyldihydrobrazileinol (Engels, Perkin, and Robinson, *loc. cit.*). At a much earlier stage of the investigation, the residue (R) mentioned in the last section was submitted to similar treatment; the ferrichloride so obtained crystallised from glacial acetic acid in slender, orange needles and was directly compared with an exceptionally pure specimen of *iso*brazilein ferrichloride trimethyl ether, with the result that no differences could be detected. The comparison was made in almost the same manner as that instituted by Crabtree and Robinson (*loc. cit.*) with a similar purpose in view and in all cases the properties of the specimens were examined side by side. It is not considered necessary to reproduce the account of these properties, since important variations from the description were not observed.

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CCLXXVIII.—*Esterification in Mixed Solvents.*

By BALWANT WASUDEO BHIDE and HERBERT EDMESTON WATSON.

PREVIOUS experiments (Bhide and Sudborough, *J. Indian Inst. Sci.*, 1925, **8A**, 89) have shown that the equation $(r - a) \log a/(a - x) - x = kt$ suggested by Goldschmidt and Udby (*Z. physikal. Chem.*, 1907, **60**, 728) gives satisfactory values for the velocity coefficient k in numerous cases of esterification of organic acids with ethyl alcohol, and thus allows for the effect of the water formed during the reaction. The question as to the actual catalytic agent is, however, still obscure. Of the theories which have been put forward (compare Lapworth, J., 1911, **99**, 1427; Rice *et al.*, *J. Amer. Chem. Soc.*, 1923, **45**, 2808; 1924, **46**, 2405; 1925, **47**, 379), that of Goldschmidt (*Z. physikal. Chem.*, 1913, **81**, 30; 1920, **94**, 233), according to which both the hydrogen ions and the undissociated molecules are assumed to act as catalysts, has given satisfactory results in explaining the enolisation of acetone, the decomposition of diazoacetates, and the esterification of certain acids with methyl and ethyl alcohols, for a range in concentration of the catalyst from 0·05 to 0·2N. As the degree of dissociation between these limits only changes by approximately 10%, the relative effects of the ions and molecules cannot be determined with great accuracy.

In order to study the question through a greater range of ionic concentration, it was decided to examine the effects obtained in the presence of non-dissociating solvents. Kailan (*Z. physikal. Chem.*, 1914, **88**, 63) has shown that the velocity coefficient for the esterification of benzoic acid by ethyl alcohol is largely increased when benzene is added, but he has not worked with solutions containing more than 75% of benzene.

In the present experiments, mixtures of *iso*amyl alcohol with benzene or ligroin have been used. As acids, suberic and *n*-butyric were selected on account of their convenient rates of esterification. The former is moderately easily soluble in *iso*amyl alcohol (5·15 g. per 100 g. of solvent), but almost insoluble in benzene and ligroin. The latter is miscible in all proportions with all three solvents.

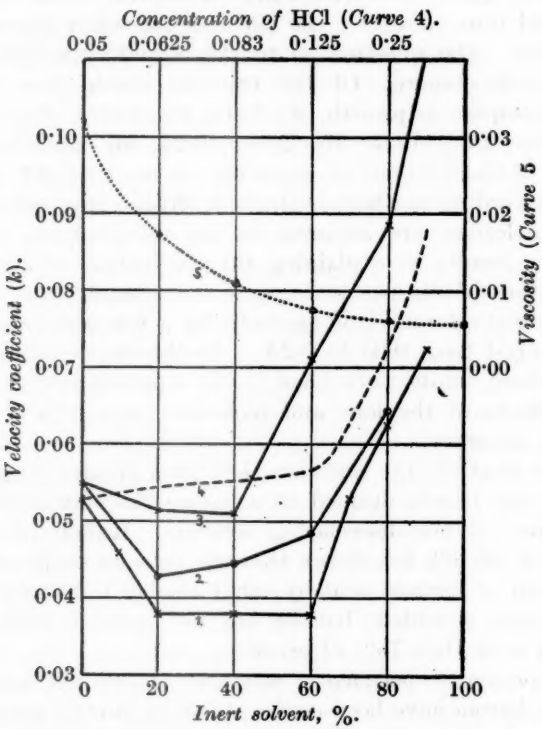
EXPERIMENTAL.

The *iso*amyl alcohol was very carefully purified and dried, the final drying agent being anhydrous copper sulphate, as metallic calcium was found to give rise to traces of ammonia which increased the conductivity. At 30°, it had d 0·8026 and specific conductivity 2×10^{-7} mho. The suberic acid had m. p. 140°; *n*-butyric

acid, b. p. 156—157°/685 mm.; and benzene, $d_4^{30°}$ 0·8658. The ligroin dried over sodium had b. p. 80—90°/685 mm., and did not decolorise bromine. Throughout the preparation and subsequent use of these materials, the utmost care was taken to exclude moisture.

The composition of mixtures is given as % by vol., and density determinations showed that the change of volume on mixing was negligible.

FIG. 1.



Curve 1. *Suberic acid–benzene.* 2. n-*Butyric acid–benzene.* 3. n-*Butyric acid–ligroin.* 4. *Suberic acid–isoamyl alcohol with varying* HCl. 5. *Viscosity:* isoamyl *alcohol–benzene.*

Several determinations of the viscosity and conductivity of the solutions were made in order to ascertain whether these properties could be correlated with the velocity coefficients.

Viscosity measurements were made with an Ostwald viscometer at 30° ± 0·05° and the results are in Table I and Fig. 1 (Curve 5).

When hydrogen chloride is dissolved in *iso*amyl alcohol, the viscosity increases regularly with the concentration, rising from 0·0321 for the pure alcohol to 0·0354 for a 0·142*N*-solution.

TABLE I.

Viscosity of mixtures of *iso*amyl alcohol and benzene.

Benzene, %	Time of flow (secs.).	$d_4^{30°}$.	η.	Benzene, %	Time of flow (secs.).	d_4^{30}.	η.
0	419·0	0·8026	0·0321	60	95·0	0·8397	0·00760
20	222·4	0·8147	0·0173	80	76·4	0·8525	0·00621
40	137·4	0·8266	0·0108	100	68·0	0·8658	0·00562

Conductivity measurements of solutions of hydrogen chloride in the anhydrous solvents were made, but were rendered difficult by the large decrease in conductivity caused by traces of water. Table II shows the effect of water upon the equivalent conductivity (Λ) of a 0·1*N*-solution of hydrogen chloride in *iso*amyl alcohol;

TABLE II.

Conductivity of 0·1*N*-*iso*amyl alcohol solutions of HCl containing water.

H_2O (mols./litre)	0·0	0·078	0·163	0·203	0·248	0·31	0·62	1·05
Λ	2·18	1·62	1·494	1·491	1·490	1·64	1·99	2·33

it will be observed that the conductivity drops rapidly to a minimum and then steadily rises. Analogous results have been obtained by Goldschmidt (*Z. physikal. Chem.*, 1915, **89**, 129) in the case of ethyl alcohol. Consistent results could only be obtained by making a fresh solution in the conductivity cell itself for each determination.

Table III gives the results obtained for *iso*amyl alcohol alone and for 20 and 40% benzene solutions.

TABLE III.

Conductivity of HCl in *iso*amyl alcohol.

HCl (*N*)	0·00565	0·0166	0·0216	0·0303	0·055	0·071	0·086	0·110	0·164
Λ	2·42	2·33	2·28	2·21	2·18	2·16	2·15	2·20	2·27

Conductivity of HCl in *iso*amyl alcohol containing 20% of benzene.

HCl (*N*)	0·0133	0·0250	0·0385	0·0425	0·0675	0·0773
Λ	1·040	0·917	0·883	0·886	0·923	0·958

Conductivity of HCl in *iso*amyl alcohol containing 40% of benzene.

HCl (*N*)	0·0171	0·0196	0·0308	0·0443	0·074	0·103	0·132
100Λ	1·43	1·36	1·27	1·33	1·53	1·83	2·22

In all these solutions Λ has a minimum value. Godlewski (*J. Chim. physique*, 1905, **3**, 432) has observed a similar minimum for the case of acetic acid in amyl alcohol.

The conductivities of solutions with a higher proportion of benzene were very low, *e.g.*, 0·088*N*-hydrogen chloride in 60% benzene solution had an equivalent conductivity of $7·1 \times 10^{-4}$ mho.

Reaction Velocity.

The rate of esterification was measured in the manner previously described (Bhide and Sudborough, *loc. cit.*) at 30° ± 0·01°. At this temperature the concentration of a 0·05*N*-solution of hydrogen chloride in *iso*amyl alcohol remained unchanged for more than 48 hours. As the reaction with suberic acid was practically complete in 7 hours, no complication was produced by reaction between the alcohol and hydrogen chloride.

According to Goldschmidt the value of r in his formula is constant for any one alcohol. It may be calculated by taking a series of readings during the course of an esterification and solving for k and r from two of the simultaneous equations so obtained. In the present case, r was determined from esterification experiments with both suberic and acetic acids, and the mean value 0·11 was found to yield values of k which were in good agreement with each other in every experiment, so that it is not necessary to give detailed results. The final values for the velocity coefficients are in all cases the mean of at least two concordant determinations.

Preliminary experiments showed that the velocity coefficient was not proportional to the concentration of catalyst but became relatively greater as the concentration increased. In all subsequent experiments the concentration of hydrogen chloride was kept as near to 0·05*N* as possible.

Table IV shows the extent of this variation for the esterification of 0·1*N*-suberic acid by *iso*amyl alcohol. The coefficients given are calculated for 0·05*N* catalyst on the assumption that the velocity coefficient is proportional to the concentration of catalyst.

TABLE IV.

Change in velocity coefficient with catalyst concentration.

HCl (*N*)	0·0045	0·012	0·050	0·100	0·220	0·464
k for 0·05*N*-HCl	0·036	0·045	0·053	0·056	0·071	0·086

Goldschmidt and Udby's formula was found not to give a constant for the highest concentration of acid, the value of k increasing with time. The figure 0·086 in the table is the initial value.

Table V shows the velocity coefficients for 0·1*N*-suberic and *n*-butyric acids in mixtures of *iso*amyl alcohol and benzene with 0·05*N*-hydrogen chloride as catalyst.

As has been pointed out by Kailan (*loc. cit.*), the quantity k, although constant in any one experiment, is not proportional to the true velocity coefficient when the composition of the solvent is altered. The general equation for a second-order reaction may be written $dx/dt = k_1Cc$, where C and c are the concentrations of

TABLE V.

Velocity coefficients of 0·1*N*-suberic and *n*-butyric acids.

	Suberic acid.		*n*-Butyric acid.	
Benzene, %.	$k \times 10^4$.	$k_1 \times 10^4$.	$k \times 10^4$.	$k_1 \times 10^4$.
0	535	535	550	550
10	458	509		
20	380	475	430	537
40	381	635	446	743
60	378	945	487	1220
70	531	1770		
80	625	3130	645	3230
90	725	7250		

the reacting substances. When one of these substances is used as solvent, as in the present case, C may be regarded as constant throughout the reaction, and k_1C may be replaced by k. The latter is the velocity coefficient of Goldschmidt and Udby's equation. The true velocity coefficient $k_1 = k/C$. If C is changed by the addition of a second solvent, this fact must be taken into account when calculating k_1. In Table V, C has been taken as unity for the pure solvent.

Fig. 1 shows diagrammatically the values of k in Table V and also the results for 0·1*N*-*n*-butyric acid in mixtures of *iso*amyl alcohol and ligroin. The curves are similar in shape and appear to exhibit breaks, but this cannot be confirmed without a large number of fresh determinations. The experimental points have been joined merely to show the general trend.

Discussion of Results.

The most striking feature of these results is the large increase in the value of k_1 as the alcohol is diluted with the neutral solvent. The values of k, on the other hand, although decreasing at first and then rising, do not fluctuate to such an extent. This suggests that the method by which k_1 has been calculated from k is inaccurate, or that there is some compensating factor which has not been taken into account, for it seems unlikely that the reactivity should increase more than ten times on the addition of a second solvent.

While the assumption that the reaction velocity is proportional to the concentration of the alcohol is probably correct in the case of an uncatalysed reaction, it does not follow that the same is true in the presence of a catalyst. In the latter case, it is quite possible that the catalyst is mainly associated with the alcohol, a certain proportion of the complexes (whether ionic or molecular) being in the active condition. If a neutral solvent, particularly one in which the catalyst is comparatively insoluble, is now added, the

relation between alcohol and catalyst may be only slightly changed. In other words, the velocity may depend upon the ratio of catalyst molecules to alcohol molecules.

Consider 50 c.c. of a 0·1*N*-solution of suberic acid in 0·1*N*-amyl-alcoholic hydrogen chloride. The velocity coefficient according to Table IV is 0·056 × 2, corresponding with the presence of a certain number of active complexes. If 50 c.c. of benzene, containing the necessary amount of suberic acid to keep the concentration constant, are now added, and it is supposed that the total number of these complexes does not alter, the number in 50 c.c. will be half the original number and the velocity coefficient will be 0·056, and not 0·053 as might be expected from the fact that the catalyst concentration is now 0·05*N*. Similarly for a 10% amyl alcohol solution, the velocity coefficient for 0·05*N* catalyst would be 0·1 times its value for 0·5*N* catalyst, or approximately 0·09. This is qualitatively in agreement with observation, as may be seen in Fig. 1: curve 4 represents the figures in Table IV for the variation of velocity coefficient with acid concentration, plotted in such a way that they show the velocity coefficient calculated as above for each mixed solvent, *i.e.*, corrected so as to show the concentration with reference to the amyl alcohol. The general shape of the later part of this curve has a distinct resemblance to the corresponding portions of the esterification curves.

If this hypothesis be correct, k represents the velocity coefficient, and not k_1.

The present results show that reaction can take place rapidly in the absence of any appreciable number of ions, but they do not afford information as to the relative effect of ions and molecules.

It has so far not been possible to explain either the diminution in k on adding small quantities of benzene, or the minimum in the conductivity curves. Attempts have been made to measure the hydrogen-ion concentration, but so far they have not been successful.

It is evident that much further work is required before more definite conclusions can be drawn, and the experiments are being continued.

Summary.

1. The velocity coefficients of esterification of suberic and *n*-butyric acids in mixtures of *iso*amyl alcohol with benzene and ligroin have been measured in the presence of hydrogen chloride as catalyst.

2. Goldschmidt and Udby's formula has been found to yield satisfactorily constant coefficients.

3. The coefficients increase very considerably on addition of

the neutral solvents, the relation between the value of the coefficient and the composition of the solution being approximately hyperbolic. A possible explanation is that the velocity depends upon the ratio of catalyst to alcohol molecules, and not upon the concentration of catalyst in the whole solution.

4. Conductivity and viscosity measurements have also been made, and it is shown that the ionisation of the catalyst is a negligible factor in determining the velocity. The conductivity of the solutions in which the reaction took place most readily was very low.

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CCLXXIX.—*Acid and Salt Effects in Catalysed Reactions. Part X. The Hydrolysis of Ethyl Acetate with Acetic Acid as Catalyst.*

By HARRY MEDFORTH DAWSON and WILLIAM LOWSON.

IN presence of a strong acid, the rate of hydrolysis of ethyl acetate in dilute aqueous solution is determined by the difference between two reaction velocities which are proportional, respectively, to the concentration of the unhydrolysed ester and to the square of the concentration of the hydrolysed ester.

The integration of the differential equation, which takes account of the two opposed reactions, leads to a formula of very complicated type (compare Harned and Pfanstiel, *J. Amer. Chem. Soc.*, 1922, **44**, 2193), and on this account it is customary to consider the reaction as non-reversible and to replace the total initial concentration of the ester by that corresponding with the ester which has been hydrolysed when the state of equilibrium is reached.

Since the experiments to be described by us are concerned, *inter alia*, with the determination of an accurate value for the catalytic coefficient of the hydrogen ion, it has seemed necessary to inquire to what extent and under what conditions the neglect of the reverse reaction affords a constant which may be taken as a measure of the true hydrolytic coefficient k_r in the equation for the reversible charge. The latter may be written

$$dx/dt = k_r(w - x)(a - x) - k'_r x^2,$$

in which w represents the molar concentration of water and a that of the total ester in the original solution.

Since under the conditions of the experiments to be described x may be neglected in comparison with w, and k'_r may be replaced

by $K_e k_r$, where K_e is the equilibrium constant, the above equation assumes the form

$$dx/dt = k_r\{w(a - x) - K_e x^2\} \quad . \quad . \quad . \quad . \quad (1)$$

The two simplified equations which have been compared with this are

$$dx/dt = k_0 w(a - x) \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

and

$$dx/dt = k_e w(a_e - x) \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

in which k_0 refers to the velocity expressed in terms of the total ester concentration, and k_e is the coefficient obtained by using the concentration of ester, a_e, which has been hydrolysed at the attainment of equilibrium.

In so far as (2) and (3) may be supposed to represent correctly the reaction velocity at different stages, the three values of dx/dt may be equated. From (1) and (2) we thus obtain

$$k_0/k_r = 1 - K_e x^2/w(a - x) \quad . \quad . \quad . \quad . \quad . \quad (4)$$

and from (1) and (3)

$$k_e/k_r = (a - x)\{1 - K_e x^2/w(a - x)\}/(a_e - x) \quad . \quad . \quad (5)$$

On the assumption that k_r is the true velocity coefficient of the hydrolytic reaction, the ratios k_0/k_r and k_e/k_r show to what extent equations (2) and (3) may be used in substitution for equation (1). When the ester concentration is small, *e.g.*, $a = 0{\cdot}05$, the difference between the coefficients is not a matter of importance, but it may be readily shown that the difference is considerable for higher ester concentrations.

The comparison we have instituted has reference to the ester concentration used in our experiments, *viz.*, $a = 0{\cdot}4$; under these conditions $w = 53{\cdot}0$, and if $K_e = 4{\cdot}0$, $a_e = 0{\cdot}3886$, corresponding with 97·15% hydrolysis. The relevant numbers are shown in Table I, from which it is apparent that equation (2) yields a

TABLE I.

Comparison of Velocity Coefficients.

x	0	0·05	0·1	0·15	0·2	0·25	0·3	0·35
k_0/k_r	1·0	0·999	0·997	0·993	0·985	0·969	0·932	0·815
k_e/k_r	1·029	1·033	1·037	1·040	1·044	1·048	1·052	1·055

" constant " which in the early stages of the reaction differs very little from the true coefficient k_r. On the other hand, equation (3) gives a " constant " which is very considerably greater than k_r, and such advantage as may be claimed for this equation is limited to the circumstance that the " constant " associated with it does not change very greatly even in the late stages of the reaction.

The relations disclosed by the above comparison have been of considerable assistance in deciding that equation (2) is to be preferred to (3) as a basis for the development of an integral formula to represent the earlier stages of the hydrolysis of ethyl acetate under the catalytic influence of acetic acid.

Results obtained in the study of the acetone–iodine reaction have shown that catalytic effects are produced by the undissociated acetic acid and the acetate ion as well as by the hydrogen ion, and if these are taken into account in the present case, the form assumed by equation (2) is

$$dx/dt = \{k_h[H^+] + k_a[A^-] + k_m[HA]\}w(a - x)$$

Experiments to be described in a subsequent paper show, however, that the coefficients k_a and k_m are very small, and that the terms $k_a[A^-]$ and $k_m[HA]$ can in general be neglected in comparison with $k_h[H^+]$ when acetic acid is used as catalyst in the absence of the corresponding salt. If b denotes the original concentration of the acetic acid, then $[H^+] = \sqrt{K(b + x - [H^+])} = \text{approx.}\sqrt{K(b+x)}$, and the previous equation becomes

$$dx/dt = k_h w\sqrt{K}(a - x)(b + x)^{\frac{1}{2}} \quad . \quad . \quad . \quad . \quad (6)$$

$$= k(a - x)(b + x)^{\frac{1}{2}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (6a)$$

By substituting $y = (b + x)^{\frac{1}{2}}$, equation (6a) becomes

$$k \,.\, dt = 2dy/(a + b - y^2)$$

which may be integrated by the method of partial fractions. We thus obtain

$$kt = \frac{1}{\sqrt{a+b}}\{\log(\sqrt{a+b} + y) - \log(\sqrt{a+b} - y)\} + \text{constant},$$

and since $y = \sqrt{b}$ when $t = 0$

$$\text{constant} = -\frac{1}{\sqrt{a+b}}\{\log(\sqrt{a+b} + \sqrt{b}) - \log(\sqrt{a+b} - \sqrt{b})\}$$

Replacing y by $(b + x)^{\frac{1}{2}}$ and transposing, we obtain

$$k = \frac{1}{t\sqrt{a+b}}\left\{\log\frac{\sqrt{a+b} + \sqrt{b+x}}{\sqrt{a+b} - \sqrt{b+x}} - \log\frac{\sqrt{a+b} + \sqrt{b}}{\sqrt{a+b} - \sqrt{b}}\right\} \quad (7)$$

This equation will be applied to experiments for which $a = 0{\cdot}4$, and $b = 0{\cdot}1$.

Preliminary observations under these conditions showed clearly that the reaction velocity increases in the early stages and this circumstance suggested a further analysis of equation (6a). By differentiation we obtain

$$dv/dx = \tfrac{1}{2}k(a - x)(b + x)^{-\frac{1}{2}} - k(b + x)^{\frac{1}{2}} \quad . \quad . \quad . \quad (8)$$

according to which the velocity passes through a maximum when $a - x = 2(b + x)$, *i.e.*, when $x = x_m = (a - 2b)/3$. If $a = nb$, x_m becomes $(n - 2)b/3$, and since this must be a positive quantity, it follows that a maximum velocity will only be obtained when the ester–acetic acid ratio is greater than 2. If $n =$ or < 2, the velocity should fall continuously as the reaction proceeds.

In terms of n and b, the initial velocity v_0 is given by

$$v_0 = knb^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

and the maximum velocity, v_m, by

$$v_m = 2k\{(n + 1)b/3\}^2 \quad . \quad . \quad . \quad . \quad . \quad (10)$$

whence for the ratio of maximum to initial velocity we obtain

$$v_m/v_0 = 2/n \, . \, \{(n + 1)/3\}^2 \quad . \quad . \quad . \quad . \quad (11)$$

according to which this ratio depends only on n or a/b. Table II shows how the relative magnitude of the maximum velocity and the point at which it occurs depend on the value of n. The values of n, x_m, and v_m/v_0 are recorded in the first, second, and fourth horizontal lines; the third line gives the % of ester, $100\,x_m/a$, which has been hydrolysed when the velocity attains its maximum value.

TABLE II.

n	2·0	3·0	4·0	5·0	6·0	10·0
x_m	0	$b/3$	$2b/3$	b	$4b/3$	$8b/3$
$100x_m/a$	0	11·1	16·7	20·0	22·2	26·7
v_m/v_0	1	1·03	1·075	1·13	1·19	1·40

EXPERIMENTAL.

The velocity measurements were made at 25°. The ethyl acetate was a fractionated research chemical which on saponification was found to contain 99·9% of ester. Preliminary observations showed that greatly increased accuracy could be obtained by the use of weight-volumetric methods and that this mode of procedure was essential in so far as the determination of the average speed at successive stages of the reaction was attempted.

In the recorded experiments, a 25 (or 10) c.c. sample of the ester solution was introduced into a weighed flask containing water and a measured quantity of phenolphthalein, the flask and its contents being re-weighed before and after the addition of the 0·1*N*-sodium hydroxide necessary to produce the tint accepted as an indication of the end-point. Using every precaution, it was found that titration results were reproducible within limits of $\pm$ 0·02 c.c. The influence of the titration error on the value of x varies with the progress of the reaction, but is in all cases such as

to warrant the belief that the accuracy of the analytical procedure was sufficient for the purpose of the inquiry.

Table III gives the detailed record of an experiment the data for which have been examined in reference to equation (7). Col. 1 gives the time in minutes, col. 2 the weight of solution titrated, and col. 3 the weight of standard alkali solution (0·0996*N*-NaOH) required. Col. 4 records the values of $(b + x)$ in mols. per litre, and col. 5 gives the values of k calculated from equation (7).

TABLE III.

$a = 0{\cdot}413$; $b = 0{\cdot}0977$.

t (mins.).	Wt. of sol. titrated.	W. of standard alkali.	$b + x$.	$k \times 10^5$.
1,645	24·934	24·462	0·1033	2·61
5,640	24·940	25·859	0·1172	2·63
9,970	24·943	29·337	0·1326	2·61
14,300	24·951	33·206	0·1481	2·61
17,160	10·006	14·875	0·1587	2·61
25,985	10·002	15·936	0·1902	2·59
33,005	10·002	20·139	0·2158	2·60
36,030	10·016	22·741	0·2262	2·59
43,120	9·993	25·169	0·2509	2·59
50,310	10·005	27·515	0·2739	2·59
64,675	9·999	31·797	0·3167	(2·57)
74,840	9·992	34·378	0·3427	(2·56)
84,860	9·987	36·710	0·3661	(2·55)
94,950	9·993	38·715	0·3859	(2·54)
106,870	9·985	40·760	0·4066	(2·52)

In accordance with the preceding analysis (compare Table I), the value of k would be expected to remain sensibly constant until about half of the original ester has been hydrolysed. As the figures in the last column of Table III indicate, this anticipation is fully realised within the limits of experimental error. The steady fall in the later (bracketed) values of k is quite in accordance with expectation.

If the experimental data for the later stages of the reaction are to be analysed with any degree of precision, it is essential that consideration should be given to the reverse reaction, but this does not necessarily imply the use of the complex integration formula (compare p. 2107). On the contrary, if the measurements of the reaction velocity are sufficiently accurate and the variations in the velocity are relatively small, the experimental results may be tested by comparing the observed average velocity for successive time intervals with the calculated velocity for the middle of each such interval. In so far as the variation of the velocity is concerned, the reaction investigated by us fulfils the stipulated requirement until the latest stages are reached, in that the effect of diminishing ester concentration is counteracted by the effect of

increasing concentration of the acetic acid. If $\bar{v} = \Delta x/\Delta t$ is the average velocity for an interval in which x increases from x_1 to x_2, and $\bar{x} = (x_1 + x_2)/2$ represents the mean value of x, then in accordance with equation (6) we have

$$\bar{v} = k_h w\sqrt{K}(a - \bar{x})(b + \bar{x})^{\frac{1}{2}} - k'_h\bar{x}\sqrt{K}(b + \bar{x})^{\frac{3}{2}}$$

and since $k_h w\sqrt{K} = k$ and $k'_h = K_e k_h$

this may be written

$$\bar{v} = k\{(a - \bar{x})(b + \bar{x})^{\frac{1}{2}} - K_e/w \,.\, \bar{x}(b + \bar{x})^{\frac{3}{2}}\} \quad . \quad . \quad (12)$$

The application of equation (12) to the experimental data is shown in Table IV. Col. 1 gives the length of the time interval (Δt) between each successive pair of readings in Table III, col. 2 the mean concentration of the ester ($a - \bar{x}$), col. 3 the mean concentration of the acetic acid ($b + \bar{x}$), col. 4 the observed mean velocity, col. 5 the velocity calculated from equation (12) with $k = 2{\cdot}61 \times 10^{-5}$ (see Table III), whilst col. 6 gives the values of k obtained by dividing the observed average velocity by $(a - \bar{x})(b + \bar{x})^{\frac{1}{2}} - K_e/w \,.\, \bar{x}(b + \bar{x})^{\frac{3}{2}}$.

TABLE IV.

Δt (mins.).	$(a - \bar{x})$.	$(b + \bar{x})$.	$\bar{v} \,.\, 10^6$ (obs.).	$\bar{v} \,.\, 10^6$ (calc.).	$k \,.\, 10^5$.
1,645	0·4102	0·1005	3·45	3·39	2·65
3,995	0·4005	0·1102	3·48	3·47	2·62
4,330	0·3858	0·1249	3·56	3·56	2·61
4,330	0·3704	0·1403	3·58	3·62	2·57
2,860	0·3573	0·1534	3·70	3·65	2·64
8,825	0·3363	0·1744	3·57	3·65	2·55
7,020	0·3077	0·2030	3·65	3·60	2·65
3,025	0·2897	0·2210	3·44	3·52	2·55
7,090	0·2722	0·2385	3·48	3·44	2·64
7,190	0·2483	0·2634	3·20	3·28	2·55
14,455	0·2154	0·2953	2·96	2·99	2·58
10,075	0·1810	0·3297	2·58	2·62	2·56
10,020	0·1563	0·3544	2·34	2·32	2·63
10,090	0·1347	0·3760	1·96	2·03	2·52
11,920	0·1145	0·3962	1·74	1·73	2·62

In reference to the above table, it may be noted that the observations cover a period of 75 days, at the end of which about 75% of the ester had been hydrolysed. The original intention was to make the successive time intervals approximately equal, but various circumstances intervened to prevent the carrying out of this proposal. The close agreement of the observed and calculated velocities shows that the reaction proceeds throughout in accordance with the requirements of equation (12). This is further shown by the constancy of the k values in the last column.

The estimated probable error in the determination of the interval velocities is about 2% and this corresponds fairly well with the

deviations of the separate k values from the mean. The arithmetic mean of all the recorded numbers is $k = 2{\cdot}60 \times 10^{-5}$, which is almost identical with the mean value of the coefficient derived from the application of the integration formula (7) to the first half of the reaction (see Table III).

In this connexion it may be noted that equation (12) involves the assumption that the hydrogen-ion concentration is given by $[H^+] = \sqrt{K(b + \bar{x})}$. If this were replaced by the more accurate value derived from $[H^+] = \sqrt{K(b + \bar{x} - [H^+])}$, the average value of k would be increased by about 0·4%. The use of the simpler expres-

FIG. 1.

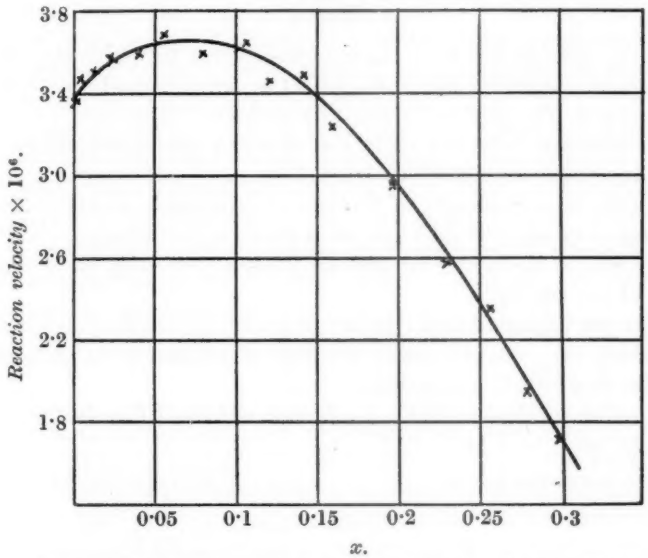

Diagram showing the variation of the reaction velocity with the proportion of ester hydrolysed.

sion is justified by the fact that the difference involved is probably within the limits of error of the mean value of k.

The observations recorded in Table IV do not actually give the initial velocity v_0. To obtain this, measurements were made with solutions for which the initial concentrations of ester and acetic acid were so adjusted that $(a - \bar{x})$ and $(b + \bar{x})$ were equal to the initial values (a and b) in the experiment of Tables III and IV. The velocity derived in this way was $v_0 = 3{\cdot}34 \times 10^{-5}$, which compares with the calculated value, $v_0 = 3{\cdot}37 \times 10^{-5}$.

The course of the reaction may be clearly visualised with the aid of the diagram. The curve on this shows the variation of the

velocity as expressed by equation (12), whilst the points represent the measured average velocities for the successive time intervals. Equations (8) and (11) give $x_m = 0{\cdot}072$ for the point at which the velocity reaches its maximum value and $v_m/v_0 = 1{\cdot}087$ for the ratio of the maximum to the initial velocity. Although direct comparison between theory and experiment is not possible, it is apparent that these numbers are in general agreement with the observed course of the reaction.

Substituting $K = 1{\cdot}85 \times 10^{-5}$ and $w = 53{\cdot}2$ in the expression $k = k_h w\sqrt{K} = 2{\cdot}61 \times 10^{-5}$, we obtain $k_h = 1{\cdot}14 \times 10^{-4}$ as the value of the catalytic coefficient for the hydrogen ion in the hydrolysis of ethyl acetate at 25°.

Summary.

An examination has been made of the extent to which the neglect of the reverse reaction interferes with the derivation of true velocity coefficients in the process of ester hydrolysis. It is shown that the usual procedure does not yield the required coefficients unless the ester concentration is very small.

Accurate measurements of the rate of hydrolysis of ethyl acetate in presence of acetic acid have been made which permit of a direct comparison of the observed and calculated velocities at successive stages of the reaction.

Under the experimental conditions (ester, 0·4 molar; acetic acid, 0·1 molar), the velocity passes through a maximum in accordance with the theoretical predictions.

The value of the catalytic coefficient obtained for the hydrogen ion at 25° is $k_h = 1{\cdot}14 \times 10^{-4}$.

THE UNIVERSITY, LEEDS. [*Received, June 7th*, 1927.]

CCLXXX.—*The Action of Hydrazines on Semicarbazones. Part III.*

By WILLIAM BAIRD and FORSYTH JAMES WILSON.

IN Part II (J., 1926, 2369) it was shown that acetophenone- and benzophenone-δ-anilinosemicarbazones on heating gave the phenylhydrazones and 4-aminourazole,* the reaction probably taking place in two stages:

$$2CRR'{:}N{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}NHPh = CO(NH{\cdot}N{:}CRR')_2 +$$

$$CO(NH{\cdot}NHPh)_2 = 2CRR'{:}N{\cdot}NHPh + CO\langle\begin{matrix}NH{\cdot}NH\\N(NH_2)\end{matrix}\rangle CO$$

* In Part II this compound was erroneously described as 1-aminourazole; the name and formula should be as now given.

From acetophenone-δ-anilinosemicarbazone, some ketazine was also produced, probably by the thermal decomposition of the intermediate carbohydrazone (compare Brown, Pickering, and Wilson, this vol., p. 107). This interpretation of the reaction has now been confirmed by heating together diacetonecarbohydrazone and diphenylcarbohydrazide, the products being acetonephenylhydrazone, 4-aminourazole and dimethylketazine. The thermal decomposition of acetone-, pinacolin-, and benzylidene-δ-anilinosemicarbazones followed the same course, no diphenylcarbohydrazide being actually isolated. In the case of acetone-δ-diphenylaminosemicarbazone, the thermal decomposition of which conformed to the general scheme, some tetraphenylcarbohydrazide, $CO(NH{\cdot}NPh_2)_2$, was actually isolated.

In the expectation of obtaining δ-anilinothiosemicarbazones, the behaviour of acetone-, acetophenone-, and dibenzyl ketone thiosemicarbazones on heating with phenylhydrazine was investigated in the usual manner. In each case, however, the phenylhydrazone and thiosemicarbazide were produced, the reaction being $CRR'{:}N{\cdot}NH{\cdot}CS{\cdot}NH_2 + NH_2{\cdot}NHPh = CRR'{:}N{\cdot}NHPh + NH_2{\cdot}NH{\cdot}CS{\cdot}NH_2$. Since acetophenone- and dibenzyl ketone semicarbazones gave excellent yields of δ-anilinosemicarbazones, the thiosemicarbazide residue is evidently more easily replaced than the semicarbazide residue.

Experimental.

Thermal Decomposition of δ-Anilinosemicarbazones.—In the preparation of δ-anilinosemicarbazide hydrochloride already described, it was found more advantageous to hydrolyse the acetophenone derivative (3·3 g.) by boiling under reflux for 20 minutes with 6% hydrochloric acid (75 c.c.) and to remove the acetophenone from the hot liquid by three extractions with carbon tetrachloride. The aqueous solution on cooling deposited the hydrochloride, the remainder of which was obtained by evaporating the filtrate under reduced pressure.

Acetone-δ-anilinosemicarbazone was prepared by mixing acetone with a concentrated aqueous solution of the hydrochloride and gradually adding a slight excess of solid potassium acetate with shaking. After cooling in ice for 5 hours, the product was collected (yield 94%). It crystallises in plates, not needles as formerly described (J., 1924, **125**, 2146). The m. p. varies somewhat with the rate of heating; this preparation had m. p. 170°, which was not depressed on admixture with the specimen previously described (Found: N, 27·1. Calc.: N, 27·2%). *Methyl ethyl ketone δ-anilino-*

semicarbazone (plates from alcohol, m. p. 137°) was prepared in the same way (Found : N, 25·4. $C_{11}H_{16}ON_4$ requires N, 25·4%).

Acetone-δ-anilinosemicarbazone was heated at 180° for 5 hours in a distillation flask with occasional evacuation until distillation ceased. The small quantity of distillate, after hydrolysis with dilute hydrochloric acid, yielded acetone on fractionation; the remainder of the liquid gave with benzaldehyde and potassium acetate a mixture of benzaldehydephenylhydrazone and benzalazine. The semi-resinous product remaining in the reaction flask was extracted with boiling absolute alcohol, which left a residue of 4-aminourazole. The alcoholic extract would not crystallise, but gave the usual diphenylcarbohydrazide colour reactions. Hence the products were acetonephenylhydrazone, dimethylketazine, and 4-aminourazole.

An intimate mixture of diacetonecarbohydrazone and diphenylcarbohydrazide (molecular quantities) was heated under the same conditions as before. The products were again acetonephenylhydrazone, dimethylketazine, and 4-aminourazole.

Pinacolin-δ-anilinosemicarbazone. The thermal decomposition was effected exactly as before. The distillate contained pinacolinphenylhydrazone and pinacolinazine, identified as such by hydrolysis with acid. The residue in the flask contained 4-aminourazole and gave the colour reactions of diphenylcarbohydrazide, which, however, could not be isolated.

Pinacolinazine was prepared by refluxing 11 g. of the ketone with 2·5 g. of hydrazine hydrate in 10 c.c. of absolute alcohol for 2 hours. After evaporation of the solution, the residual oil was dried over potassium carbonate and distilled; it was an almost colourless oil, b. p. 213—216°, 103°/17 mm., smelling somewhat like acetamide, insoluble in water and easily hydrolysed on boiling with acid (yield 77%) (Found : N, 14·3. $C_{12}H_{24}N_2$ requires N, 14·3%).

Benzylidene-δ-anilinosemicarbazone was heated for 1 hour at 230°. Since benzaldehydephenylhydrazone decomposes at about this temperature, the reaction was carried out under reduced pressure in a flask of the Anschütz type, in the collar of which a distillate, which soon solidified, collected. The whole reaction mass was extracted with boiling absolute alcohol; benzaldehydephenylhydrazone passed into solution whilst 4-aminourazole, the only other product, remained undissolved.

Acetone-δ-diphenylaminosemicarbazone. The reaction was carried out as usual: 4 hours' heating at 190—195°. The distillate on hydrolysis with hydrochloric acid gave acetone, diphenylhydrazine hydrochloride, and hydrazine hydrochloride. The dark residue in the flask was extracted with boiling absolute alcohol and then with

boiling water; the alcoholic extract on concentration deposited small needles of tetraphenylcarbohydrazide (Acree, *Ber.*, 1903, **36**, 3157) (Found: N, 14·4, 14·3. Calc.: N, 14·2%), and evaporation of the aqueous extract left 4-aminourazole. The products were therefore acetonediphenylhydrazone, dimethylketazine, 4-aminourazole, and tetraphenylcarbohydrazide.

Action of Phenylhydrazine on Thiosemicarbazones.—Molecular quantities of the reactants were heated in toluene solution or suspension at 135°.

Acetonethiosemicarbazone (6½ hours). A little ammonia was evolved, but the only products isolated were thiosemicarbazide, acetonephenylhydrazone, and a little unaltered substance.

Acetophenonethiosemicarbazone (5 hours). This compound dissolved completely and after some time thiosemicarbazide began to separate; some hydrogen sulphide and ammonia were evolved. The substances isolated were thiosemicarbazide, acetophenonephenylhydrazone, and a small quantity of an orange-coloured *substance*, m. p. 171—172°.

Dibenzyl ketone thiosemicarbazone (which crystallises in silvery leaves, m. p. 165—166°, from alcohol or benzene), was obtained by refluxing 2·1 g. of the ketone in 15 c.c. of alcohol with 0·9 g. of thiosemicarbazide in the minimum quantity of hot water for ¾ hour (Found: N, 14·9. $C_{16}H_{17}N_3S$ requires N, 14·8%). The reaction with phenylhydrazine (4 hours) gave thiosemicarbazide, dibenzyl ketone phenylhydrazone, and some unaltered substance only.

In conclusion, we wish to thank the Carnegie Trust for the Universities of Scotland for a research grant which has partly defrayed the cost of this work. We wish also to thank the Governors of this College for a research assistantship which has enabled one of us (W. B.) to share in the investigation.

THE ROYAL TECHNICAL COLLEGE,
GLASGOW.

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CCLXXXI.—*The Systems* B_2O_3–SO_3–H_2O *and* B_2O_3–P_2O_5–H_2O.

By MIRIAM LEVI and LIONEL FELIX GILBERT.

(i) *The System* B_2O_3–SO_3–H_2O.

MERZ (*J. pr. Chem.*, 1866, **99**, 81) stated that when equal weights of boric and concentrated sulphuric acids were heated to constant weight at 250—280° a substance was obtained of composition $5B_2O_3,2SO_3,2H_2O$. Gmelin reported (*Ann. Supp.*, 1867, **5**, 165)

that boron trioxide and boric acid dissolved extensively in concentrated sulphuric acid on heating, and that on cooling a thick syrup was obtained which deposited hydrates of boric acid on standing in moist air. Schultz-Sellack (*Ber.*, 1871, **4**, 12) found that the solution of boric acid in concentrated sulphuric acid gave on evaporation a viscous or glassy mass, which was not of constant composition. If, however, the sulphuric acid solution was treated with sulphur trioxide, or if boron trioxide was added to fuming sulphuric acid, leafy crystals, of composition $B_2O_3,3SO_3,H_2O$, were obtained on evaporation.

D'Arcy (J., 1889, **55**, 155) could not confirm the existence of Merz's or Schultz-Sellack's compounds. He reports that on mixing boric acid with excess of sulphur trioxide a violent reaction occurs; on heating the mixture at 100° till no more fumes are evolved and then cooling, a white substance separates of composition $B_2O_3,6SO_3,3H_2O$. Herz (*Z. anorg. Chem.*, 1903, **34**, 205) has made solubility measurements of boric acid in four different concentrations of sulphuric acid, 9*N* being the highest; no examination of the solid phases was made.

In the present work, a partial survey of the condensed ternary system has been made at 25° and 45° by the Schreinemakers method, supplemented by direct analyses of the solid phases. None of the above compounds has been found to exist under our experimental conditions, but the new compounds $B_2O_3,SO_3,4H_2O$ and $3B_2O_3,SO_3,3H_2O$ appear to be definitely characterised.

The reactants supplying the components were, in addition to water, concentrated sulphuric acid, fuming sulphuric acid, boric acid, and a specimen of powdered boron trioxide containing about 13% of water. These substances were in each case of a satisfactory degree of purity.

The boric–sulphuric acid mixtures examined were analysed by Herz's method (*Z. anorg. Chem.*, 1903, **33**, 353), which was tested and found to be very accurate, although the few solubilities recorded by that author do not agree with ours (see below), possibly owing to the fact that in determining them he used a less accurate method (compare Kendall and Andrews, *J. Amer. Chem. Soc.*, 1921, **43**, 1550). The procedure was to titrate suitably diluted solutions with 0·1*N*-sodium hydroxide in the presence of *p*-nitrophenol as indicator until the first yellow colour appeared, corresponding with the neutralisation of the sulphuric acid; 10 c.c. of a neutral, saturated solution of mannite and two drops of phenolphthalein solution were then added, and the titration was continued until a definite pink colour persisted for 3 minutes. This latter amount of alkali was equivalent to the boric acid present.

The solubility determinations were complicated, when high concentrations of sulphuric acid were concerned, by the ease with which highly supersaturated solutions were obtained, even when solution was effected at room temperatures. This tendency was especially marked in the region relating to the solid phase, $B_2O_3,SO_3,4H_2O$.

In some cases, solutions stood for several weeks before any solid phase commenced to separate, and the further precipitation was also very slow. None of the usual methods for overcoming this type of difficulty, *viz.*, cooling, heating, or the addition of foreign bodies or of the appropriate solid phase, seemed to have any marked effect.

Three methods of obtaining the necessary data for the ternary diagram were employed.

(*a*) The well-known method of agitating in a thermostat sealed glass tubes containing the reactants mixed in suitable proportions was employed for low concentrations of sulphuric acid, where equilibrium was easily attained. As soon as a tube was opened, the liquid and the wet solid were rapidly sampled and the samples were transferred to a specific-gravity bottle in the thermostat and to a weighing bottle, respectively.

(*b*) The reactants were stirred with dry air in an apparatus similar to that used by Donnan and White (J., 1911, **99**, 1788), the Gooch crucible used by these authors for separating solid and liquid being here replaced by a glass filter-funnel with a permanently fixed filter-plate of fritted glass. This method was used with some of the higher concentrations of (non-fuming) sulphuric acid, where the attainment of equilibrium was too slow by the tube method.

(*c*) The reactants were placed in a glass bottle of about 500 c.c. capacity, fitted with a glass stirrer passing through a mercury seal. After long stirring, the solid was allowed to segregate and samples of liquid and solid were taken. This method was used for mixtures containing fuming sulphuric acid, and for some other mixtures of high viscosity.

Compositions of saturated solutions and of their respective wet solids are shown in Table I and Fig. 1 for 25°, and in Table II for 45°. Although Herz's solubilities were determined at 26°, they are consistently lower than our values for 25°; *e.g.*, the concentration of boric acid in 8·75*N*-sulphuric acid is 0·092*N* (Herz) and about 0·37*N* by interpolation from our results. Areas corresponding to three distinct solid phases will be observed in Fig. 1, *viz.*, $B_2O_3,3H_2O$ (*i.e.*, H_3BO_3), $B_2O_3,SO_3,4H_2O$, and $3B_2O_3,SO_3,3H_2O$, but there is no evidence here for any of the ternary compounds described by other authors. On plotting the 45°-data, a similar

Table I.

	Solutions. Composition (g./100 g.).		Wet solids. Composition (g./100 g.).		
$d_4^{25°}$.	SO_3.	B_2O_3.	SO_3.	B_2O_3.	Solid phase.
1·017	0·00	3·08*			
1·032	1·96	2·87	0·70	35·76	
1·039	2·90	2·79			
1·088	9·12	2·18	4·82	28·82	
1·112	11·85	2·00			
1·160	17·56	1·54			
1·270	28·82	1·04			
1·284	30·62	0·97	19·90	20·26	
1·305	32·78	0·87	18·94	24·78	
1·412	41·78	0·71	30·33	15·98	H_3BO_3.
1·446	44·44	0·68	27·74	21·60	
1·479	46·80	0·65	26·68	24·84	
	53·94	1·46	3·89	52·19	
	54·89	1·47			
1·625	55·84	2·69	47·22	10·79	
	54·66	6·09			
	54·16	7·17	35·30	23·98	
1·668	53·50	8·12	37·80	22·30	
	55·74	7·70	45·03	20·01	
1·617	54·73	10·32	48·19	17·76	
	54·20	11·73			$B_2O_3,SO_3,4H_2O$.
	51·87	15·45	49·34	18·02	
	47·27	20·93			
	51·87	21·85			
	52·89	21·06	38·72	40·64	
	57·32	18·34	41·47	38·54	
	61·44	16·07	43·71	37·34	
	63·36	15·23			
	70·02	12·00	52·61	30·05	$3B_2O_3,SO_3,3H_2O$.
1·882	73·66	10·39	59·50	24·90	
	86·24	5·07			
	86·50	4·96			
	87·72	4·82	43·43	43·45	

* In agreement with Kendall and Andrews (*loc. cit.*).

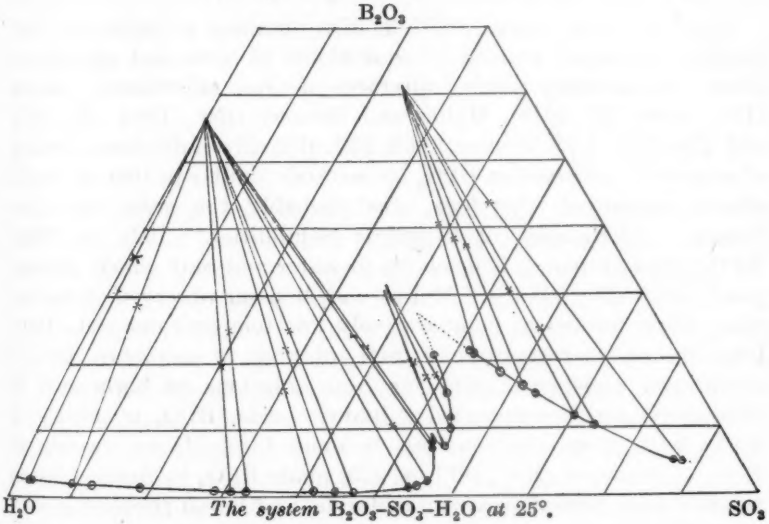
Table II.

	Solutions. Composition (g./100 g.).		Wet solids. Composition (g./100 g.).		
$d_4^{45°}$.	SO_3.	B_2O_3.	SO_3.	B_2O_3.	Solid phase.
1·023	0·00	5·17			
1·029	0·47	5·07	0·13	38·37	
1·036	1·93	4·83	0·71	34·57	
1·086	8·58	3·74	4·86	28·88	
1·097	10·18	3·51	5·78	26·54	H_3BO_3.
1·231	25·48	1·89	15·48	23·33	
1·446	44·87	0·13	33·73	13·98	
1·628	52·25	7·07	37·81	20·52	
1·671	54·13	8·33	45·45	19·83	
1·685	56·65	6·14	49·50	15·21	
	60·89	4·89	49·49	17·89	$B_2O_3,SO_3,4H_2O$.
	62·66	6·85	47·35	21·05	
1·800	57·22	13·56			
	59·87	23·60	41·08	35·18	
	57·70	19·25	41·34	40·29	$3B_2O_3,SO_3,3H_2O$.
	60·43	17·99	46·64	35·66	

solubility curve to that at 25° is obtained, but the tie-lines corresponding to the two new compounds are not so satisfactorily convergent. The attainment of equilibrium was too slow for more satisfactory data to be obtained, but it is considered that there is little doubt that the above compounds are also obtained at 45°. The quite characteristic appearances of the solid phases were also similar to those obtained at 25°.

Samples of the two new solids, prepared by the interaction of boric acid with 88% sulphuric acid, and of boron trioxide (87%)

FIG. 1.



The system B_2O_3–SO_3–H_2O *at* 25°.

with concentrated sulphuric acid, respectively, and kept in desiccators on carefully dried porous plates, gave the following analyses:

	$B_2O_3,SO_3,4H_2O$.				$3B_2O_3,SO_3,3H_2O$.			
	I.	II.	III.	Calc.	I.	II.	III.	Calc.
% SO_3	36·6	36·1	36·6	36·0	22·1	25·4	24·9	23·3
% B_2O_3	31·2	32·3	32·0	31·5	64·8	61·9	59·5	61·0

It is considered that discrepancies between observed and calculated results can fairly be ascribed to a certain amount of hydrolysis which may have occurred on sampling, and also to the difficulty of draining the viscous adherent liquids, the viscosity of which is especially high in the case of the second compound.

$B_2O_3,SO_3,4H_2O$ is a white, finely-divided, crystalline substance; $3B_2O_3,SO_3,3H_2O$ consists of larger, colourless crystals. Both compounds rapidly absorb moisture from the atmosphere, with consequent decomposition.

Viscosities of Solutions of Boric Acid in Concentrated Sulphuric Acid.—A few determinations were made at 25° of the viscosities of solutions of boric acid in concentrated sulphuric acid compared with that of the solvent, by the capillary flow method. No great accuracy is claimed for these measurements, which, however, help to emphasise some of the difficulties experienced when working with this system. The results obtained were:

% H_3BO_3	0	8·5	15·9	24·5	30·0	37·6	42·7
Relative time of flow	1	3·96	12·5	40·1	84·0	219	440

(ii) *The System* B_2O_3–P_2O_5–H_2O.

Vogel (*Z. anal. Chem.*, 1870, **9**, 376) obtained a compound containing "an equal number of equivalents of boric and phosphoric acids" by strongly heating mixtures of these substances. Meyer (*Ber.*, 1889, **22**, 2919), Mylius and Meusser (*Ber.*, 1904, **37**, 397), and Prescher (*Arch. Pharm.*, 1904, **242**, 199) all obtained a substance of empirical composition BPO_4 by methods similar to that of Vogel, whose compound, therefore, was probably the same (compare Comey, "Dictionary of Chemical Solubilities," 1921, p. 668). BPO_4, thus prepared, is insoluble in water and only slowly decomposed by boiling alkalis. Mylius and Meusser observed, however, that, when formed at comparatively low temperatures (80—100°) from the above reactants, or from solutions of metaboric acid in acetic and phosphoric acids or from solutions of boric acid in phosphoric and concentrated sulphuric acids, BPO_4 is soluble in water with decomposition, but becomes insoluble on heating to 400°. Gustavson (*Ber.*, 1871, **4**, 975) made BPO_4 by heating boron trioxide with phosphorus pentachloride, and boron trichloride with phosphorus pentoxide. Apparently here, too, the soluble compound was first formed and became insoluble on further heating.

The ternary system B_2O_3–P_2O_5–H_2O at 25° has now been partially investigated, and BPO_4 occurred as the solid phase in one of the regions under examination.

Well-boiled syrupy phosphoric acid, free from phosphorous acid, was employed as the source of phosphorus pentoxide, and was suitably diluted as required. The boric acid and boron trioxide used were similar specimens to those mentioned previously.

On examination of the literature, Kolthoff's method (*Chem. Weekblad*, 1922, **19**, 449) appeared to be the most suitable for the rather difficult determination of mixtures of boric and phosphoric acids, but it was found not to give sufficiently accurate results. In addition to the difficulty of distinguishing between various shades of pink, it was found that the titration value for the phosphoric acid end-point varied with the amount of boric acid present

if the titration was carried on until the same p_H value was obtained in each case. Whilst retaining the use of sodium citrate and Kolthoff's p_H value for the total-acid end-point, which was found to be correct and unaffected by the relative amounts of the acids, a new procedure was adopted. 0·1*N*-Mixtures of known composition of boric and phosphoric acids were made up, 10 c.c. of 40% sodium citrate solution and thymol-blue were then added, followed by the appropriate amount of 0·1*N*-sodium hydroxide to convert all the phosphoric acid to the secondary sodium salt. The p_H numbers acquired by the solutions were then determined by comparison with a colour chart, and plotted against the % of boric acid molecules in the total acid molecules present.

The correction graph was plotted from the following data, of which the accuracy is considered sufficient for the purpose :

% H_3BO_3.....	100	96	82	70·5	58	52	40·5	35	26·3	15·5	0
p_H	8·2	8·3	8·4	8·5	8·6	8·7	8·8	8·9	9·0	9·1	9·2

In the analysis of an unknown mixture the % of boric acid was first determined roughly and the corresponding p_H number read off the graph. Exact determinations were then made on 25 c.c. of another sample by titrating with caustic soda (in presence of sodium citrate and thymol blue) to this p_H number, thus allowing the amount of phosphoric acid to be calculated; 10 c.c. of a saturated solution of mannite were then added and the solution was titrated until the colour corresponding to p_H 8·7 lasted for at least a minute. This latter volume of sodium hydroxide was equivalent to the boric acid present. A test of the method over a wide range of relative concentrations of the acids indicated that it gave very accurate results.

The first two methods employed in the preceding system were found suitable for obtaining the solubility and wet-solid data. Some difficulty was experienced in filtering satisfactorily mixtures made with high concentrations of phosphoric acid. Large quantities of boric acid and boron trioxide will dissolve in such phosphoric acid solutions with the formation of clear liquids from which a new, very finely divided, solid phase slowly separates. This coagulates slightly and settles after 3 or 4 days, but still passes through filters of average pore diameter 35—40 $\times$ 10^{-4} and in some cases even 4—5 $\times$ 10^{-4} cm.

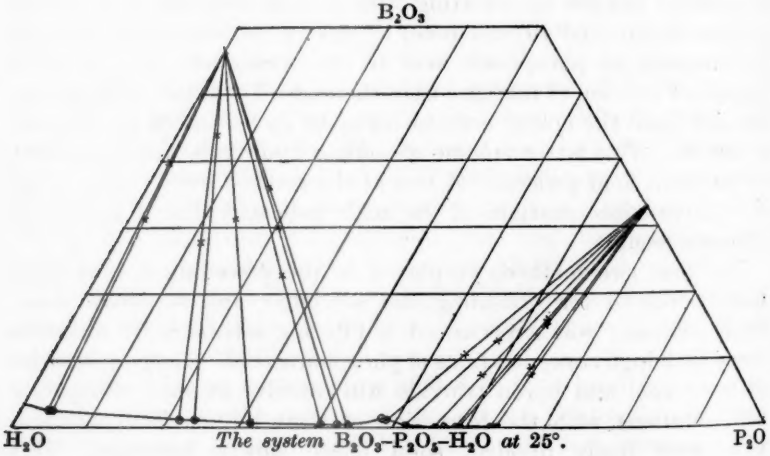
The results obtained are shown in Table III and partly in Fig. 2. The solid phase in equilibrium with solutions containing up to about 48% of P_2O_5 is boric acid, after which BPO_4 or some polymeride is formed. The BPO_4 thus obtained is the water-soluble variety. Attempts to prepare a pure dry specimen have so far

TABLE III.

	Solutions. Composition (g./100 g.).		Wet solids. Composition (g./100 g.).		
$d_4^{25°}$.	P_2O_5.	B_2O_3.	P_2O_5.	B_2O_3.	Solid phase.
1·042	3·63	2·55	1·23	39·80	H_3BO_3.
1·048	4·34	2·53	2·04	31·35	
1·190	21·51	1·12	11·09	27·91	
1·215	23·66	1·05	5·39	43·86	
1·281	31·01	0·62	14·10	31·03	
1·391	40·39	0·45	24·28	22·89	
	42·60	0·68	20·13	30·03	
1·434	43·70	0·68	16·11	35·78	
1·504	48·08	1·27	45·62	13·59*	
1·516	48·51	1·20			BPO_4.
	48·89	1·11	54·43	10·49	
	51·52	0·23	57·81	12·70	
	55·37	Concentration too low to be titrated.	58·12	7·50	
	56·99				
	58·35		62·73	15·9	
1·645	58·68		62·81	15·02	
	62·81		64·06	8·95	
1·722	63·43		64·40	7·94	

* Apparently point of inversion.

FIG. 2.



The system B_2O_3–P_2O_5–H_2O *at* 25°.

been unsuccessful. BPO_4 retains the viscous supernatant liquid very strongly and is rapidly attacked by atmospheric moisture. It appears to be a white, finely-divided powder.

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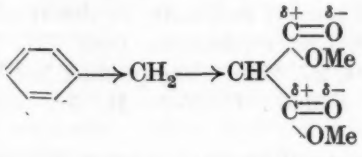
[*Received, June 7th*, 1927.]

CCLXXXII.—*The Nature of the Alternating Effect in Carbon Chains. Part XXI. The Directive Influence of the Groups* $-CH_2\cdot CH(CO_2Me)_2$, $-CH{:}C(CO_2Me)_2$, $-C(CO_2Me){:}CH_2$, *and* $-CH{:}CH\cdot CH{:}C(CO_2Me)_2$ *in Aromatic Substitution.*

By John William Baker and Alfred Eccles.

It has already been shown (Baker and Wilson, this vol., p. 842) that mechanisms depending on complete co-valency changes between the side-chain and the benzene nucleus probably play, at the most, a subsidiary part in the propagation of meta-orienting influences. Thus, electron attraction due to the integral positive charge on the nitro-group is more readily propagated to the nucleus in the ω-nitroethyl than in the corresponding ω-nitrovinyl side-chain. In the present communication, an attempt is made to confirm the previous conclusion by a study of the nitration of the analogous compounds, methyl benzylmalonate (I) and methyl benzylidenemalonate (II), in which the *gem*-dicarbomethoxyl grouping replaces the nitro-group of the previous cases. On the view that the meta-orienting influence of the carboxyl group is due to the presence of a permanent fractional dipole in the resting state of the group (Baker and Ingold, this vol., p. 832), it is to be expected that the effects produced would be much smaller in magnitude than those due to the integral dipole charge on the nitro-group.

Again, however, on any mechanism of meta-substitution which depends on the alternation of single and double bonds, a larger proportion of meta-nitration should occur in the unsaturated compound (II), in which there is an unbroken conjugated system extending from the polar group throughout the nucleus, than in the corresponding saturated compound (I). Actually, in confirm-

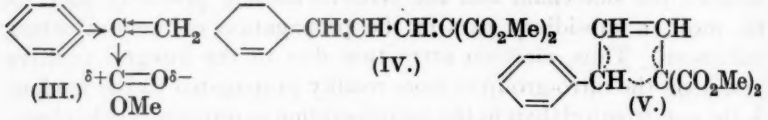
(I.)  (II.)

ation of previous results, we find the reverse to be the case, since, on nitration, methyl benzylmalonate yields 8% of meta-derivative, whilst methyl benzylidenemalonate yields only 3%.* Thus, here

* This value is somewhat higher than that expected (1—2%). It is possible that addition of nitric acid to the double bond precedes nitration and slightly increases the proportion of meta-isomeride produced.

also the electron attraction due to the fractional positive charge on the carboxyl groups is neutralised in passing through the field of the double bond.

As in the case of the nitro-compounds previously studied, the possibility of the double linking itself acting as a dominating electron-source towards the nucleus was negatived by a study of the nitration of methyl atropate (III), in which the double bond is no longer in the path of transmission from the (single) carbomethoxyl group. We find that, on nitration, this ester yields about 5% of meta-isomeride, although, owing to the small amount of material available, the figure must be considered as approximate only.



One other case was investigated, *viz.*, that of methyl cinnamylidenemalonate (IV). The point of interest here is that there might be the possibility of valency tautomerism in the side-chain leading to the cyclic form (V), in which electron-strain might conceivably be transmitted to the nucleus through two carbon atoms only, *via* the $\alpha : \delta$ partial valency, and the proportion of *m*-isomeride produced might then be more or less comparable with that obtained on nitration of methyl benzylmalonate. Actually, however, we find no evidence of this type of transmission, since the proportion of *m*-isomeride produced is less than 1%. The electron attraction of the carbomethoxyl group is thus completely neutralised by the fields of the unsaturated chain in (IV).

Experimental.

A. *Preparation of Materials.*

Methyl Benzylidenemalonate.—This was obtained by the condensation of benzaldehyde and methyl malonate, as described by Claisen and Crismer for the ethyl ester (*Annalen*, 1883, **218**, 132; compare Liebermann, *Ber.*, 1894, **27**, 289). The product had b. p. 174—177°/15 mm., m. p. 41° (Found: C, 65·6; H, 5·5. Calc.: C, 65·4; H, 5·5%).

The methyl *o*-, *m*-, and *p*-nitrobenzylidenemalonates were obtained by the condensation of the appropriate nitrobenzaldehyde with methyl malonate in the presence of piperidine as a condensing agent (compare Knoevenagel, *Ber.*, 1898, **31**, 2593).

Methyl p-*Nitrobenzylidenemalonate.*—A mixture of *p*-nitrobenzaldehyde (7·6 g.), methyl malonate (6·6 g.), and two drops of piperidine was heated to 60° for 6 hours. On cooling, the mixture

solidified, and the *nitro-ester* was recrystallised from hot alcohol; needles, m. p. 136—137° (Found: C, 54·4; H, 4·2. $C_{12}H_{11}O_6N$ requires C, 54·3; H, 4·2%). The yield is quantitative.

Methyl m-*nitrobenzylidenemalonate*, prepared similarly but in smaller yield from *m*-nitrobenzaldehyde, has m. p. 99—100° (Found: C, 54·2; H, 4·2%).

Methyl o-*nitrobenzylidenemalonate*, m. p. 65—66° (Found: C, 54·3; H, 4·3%).

Methyl benzylmalonate was prepared by esterification of the pure acid with methyl alcohol and hydrogen chloride.

Methyl o-*Nitrobenzylmalonate.*—*o*-Nitrobenzylmalonic acid (Reissert, *Ber.*, 1896, **29**, 644) was esterified through its silver salt. The *methyl* o-*nitrobenzylmalonate* was obtained as a pale yellow, viscous oil, which did not solidify on cooling to −10°, and could not be purified by distillation (Found: C, 53·8; H, 5·1. $C_{12}H_{13}O_6N$ requires C, 53·9; H, 4·9%). On oxidation with boiling 2% permanganate, it gave an acid product contaminated with gummy material in 73·3% yield (calculated as *o*-nitrobenzoic acid). By crystallisation from ether, this was shown to contain *o*-azoxybenzoic acid. Reissert (*loc. cit.*) records the formation of the latter compound by the oxidation with permanganate of 1-hydroxyindole-2-carboxylic acid formed from *o*-nitrobenzylmalonic acid by the action of potash.

Methyl m-*Nitrobenzylmalonate.*—To a solution of 4·6 g. of sodium in 50 g. of methyl alcohol, 26·4 g. of methyl malonate were added, quickly followed by a saturated solution of 17·15 g. of *m*-nitrobenzyl chloride in methyl alcohol; the mixture was heated on the steam-bath for ½ hour and filtered from sodium chloride and the *methyl di*-m-*nitrobenzylmalonate* formed as a by-product. The salt was extracted with cold water, and the dried residue crystallised from benzene; m. p. 162—162·5° (Found: C, 56·9; H, 4·6. $C_{19}H_{18}O_8N_2$ requires C, 56·7; H, 4·5%). The alcoholic mother-liquor was concentrated, poured into water, and extracted with ether. After drying the extract and evaporating the ether, the excess of methyl malonate was separated by distillation under reduced pressure. The residue, which cannot be distilled without decomposition, was dissolved in alcohol, and the solution saturated with ammonia. After standing for several days, m-*nitrobenzylmalonamide* separated as a flocculent precipitate. After several crystallisations from water, it had m. p. 203° (Found, by microcombustion: C, 51·0; H, 4·4. $C_{10}H_{11}O_4N_3$ requires C, 50·6; H, 4·6%). The amide was hydrolysed by heating at 100° with a slight excess of 10% caustic soda. On acidification of the cooled solution, m-*nitrobenzylmalonic acid* separated, and after crystallisation from water it had m. p. 164° (decomp.) (Found, by micro-

combustion: C, 50·5; H, 4·0. $C_{10}H_9O_6N$ requires C, 50·2; H, 3·8%). A further small quantity of the acid may be obtained by extracting the mother-liquors with ether. The yield of recrystallised acid was 2 g. Conversion of the crude methyl *m*-nitrobenzylmalonate into the amide is necessary, as treatment of the ester itself with alcoholic potash yields a very tarry product. The *m*-nitrobenzylmalonic acid was esterified through its silver salt, and *methyl* m-*nitrobenzylmalonate* obtained as a pale yellow, viscous oil, which did not solidify on cooling to −10° (Found: C, 54·2; H, 5·1%). On oxidation with boiling 2% potassium permanganate, it gave *m*-nitrobenzoic acid, m. p. 139°, in 90% yield.

Methyl p-*nitrobenzylmalonate*, m. p. 82·5—83·5° (Found: C, 53·85; H, 5·0%) was isolated from the reaction products by crystallisation from methyl alcohol (compare Section C). On oxidation, it gave *p*-nitrobenzoic acid, m. p. 237—239°, in 99% yield.

Methyl Cinnamylidenemalonate.—This was obtained by esterification of the acid (compare Liebermann, *Ber.*, 1895, **28**, 1439) by the method of Thiele and Meisenheimer (*Annalen*, 1899, **306**, 253) and had m. p. 67° (Found: C, 68·1; H, 5·9. Calc.: C, 68·3; H, 5·7%).

The isomeric nitro-derivatives were prepared by condensation of the appropriate nitro-cinnamaldehyde with methyl malonate in the presence of piperidine.

Methyl m-*Nitrocinnamylidenemalonate.*—A mixture of 8·85 g. of *m*-nitrocinnamaldehyde (Kinkelin, *Ber.*, 1885, **18**, 484), 6·6 g. of methyl malonate, and two drops of piperidine was heated to 60—70° for 5 hours. The cooled mixture, when treated with a few c.c. of ether and scratched, partly solidified. The separated crystals were washed with ether, recrystallised from alcohol, and obtained as felted needles, m. p. 125—126° (Found: C, 57·9; H, 4·6. $C_{14}H_{13}O_6N$ requires C, 57·7; H, 4·5%). The yield was small (about 15%). On oxidation with potassium permanganate, it gave *m*-nitrobenzoic acid, m. p. 129—132° (mixed m. p. 136—139°) in 76% yield.

Methyl o-*nitrocinnamylidenemalonate*, obtained in a similar manner from *o*-nitrocinnamaldehyde, and crystallised from methyl alcohol, had m. p. 114° (Found, by micro-combustion: C, 57·7; H, 4·6%). On oxidation it gave *o*-nitrobenzoic acid, m. p. 133—137° (mixed m. p. 139—141°), in 80% yield.

Methyl p-*nitrocinnamylidenemalonate* has m. p. 146—147° after crystallisation from methyl alcohol (Found: C, 57·8; H, 4·7%). On oxidation it gave *p*-nitrobenzoic acid, m. p. 229—231°, in 77% yield.

Methyl Atropate.—Tropic acid was converted into atropic acid by

the method of Hesse (*J. pr. Chem.*, 1901, **64**, 287), who, however, gave no details. The tropic acid (10 g.) was refluxed with 60 c.c. of a 50% aqueous solution of potassium hydroxide for 40 minutes, the solution extracted with ether, acidified with hydrochloric acid, and again extracted with ether. The crude atropic acid obtained from this dried ethereal extract was purified by crystallisation (twice) from dilute alcohol. The acid (4·5 g.) was dissolved in a large volume (1200—1500 c.c.) of very dilute ammonia solution, boiled to expel the excess of ammonia, and a slight excess of a hot solution of silver nitrate added. On cooling, the silver salt crystallised out, and was filtered and washed in succession with water, alcohol, and ether. Treatment of the dry silver salt with an excess of methyl iodide yields the *methyl atropate* in an almost pure state as a colourless, mobile liquid, b. p. 95—98°/6 mm. (Found: C, 73·6; H, 6·2. $C_{10}H_{10}O_2$ requires C, 74·1; H, 6·2), which polymerises on keeping.

B. *Conditions of Nitration.*

In all cases, the ester was slowly added at the rate of 1—2 g. per hour to about 10 times its quantity of nitric acid (*d* 1·49) at −15—−10°. Isolation of the product was effected by pouring on crushed ice, exactly neutralising the solution, first with 10% sodium hydroxide solution and finally with sodium carbonate solution, filtering off any solid product, and extracting the mother-liquors with ether. Special precautions were necessary in the case of methyl cinnamylidenemalonate (see Section C).

C. *Details relating to Individual Cases and Determination of the Proportions of the Isomerides formed.*

Since the methods employed in the separation of the isomerides are those which have been described in detail in earlier papers in this series, details of procedure are omitted in the following pages.

Nitration of Methyl Benzylmalonate.—In this case, it was found that the yield of mixed acids obtained by oxidation of the nitration mixture was only about 80—85% of that calculated from the percentage oxidation yields of the pure isomerides (compare Section A) and their estimated relative proportions. This may be due to the *o*-nitrobenzylmalonate being converted into an indole derivative under the influence of alkali (Reissert, *loc. cit.*; compare p. 2127). The proportion of *m*-nitro-ester in the nitration mixture, as calculated from the quantity of *m*-nitrobenzoic acid isolated, is probably too low, since the total oxidation yield is less than the calculated yield, but it is still considerably greater than that present in the nitration of the benzylidenemalonate. The authors are of the opinion that the percentage of *m*-nitrobenzoic acid isolated from

the mixed acids obtained on oxidation represents fairly closely the proportion of meta-derivative formed by nitration. The presence of the azoxybenzoic acid did not interfere with the separation of the mixed acids, except that sometimes it was found necessary to crystallise the *p*-acid from water.

(Expt. 31.) The yield of mononitro-compounds was 93% (Found: C, 53·4; H, 4·9. Calc. for $C_{12}H_{13}O_6N$: C, 53·9; H, 4·9%), a further 2% of the material being accounted for as acid products produced by oxidation. On oxidation, the mixed nitro-compounds yielded acids in 70% yield, which on separation by the usual method gave nitrobenzoic acids thus: para-, m. p. 234° (either alone or mixed), 70·4%; meta-, m. p. 128—135° (mixed m. p. 141°), 7·5%; ortho- (by difference), 22·1%.

A second portion of the same nitration product was crystallised from methyl alcohol, whereby 58·8% of practically pure methyl *p*-nitrobenzylmalonate, m. p. 82°, was isolated. On oxidation of the residue, some accidental loss occurred and only a 64% yield of mixed nitrobenzoic acids was obtained; these comprised: para-, m. p. 220—223°, 30%; meta-, m. p. 124—127° (mixed m. p. 138°), 16·5%. Hence the composition of the whole nitration mixture was: para-, 71·3%; meta-, 6·8%; ortho- (by difference), 21·9%.

(Expt. 33.) The yield of mono-nitration products was 93% (Found: C, 54·2; H, 4·9%), from which 56% of pure methyl *p*-nitrobenzylmalonate was isolated by crystallisation. The residues gave a mixture of acids (*M*, by titration, 165) in 72% yield, which on separation was found to contain: para-, m. p. 233—235°, 19·2%; meta-, m. p. 123—128° (mixed m. p. 133—137°), 20·9%; ortho- (by difference), 59·9%; whence the composition of the nitration mixture was: para-, 64%; meta-, 9%; ortho- (by difference), 27%.

(Expt. 34.) The yield of mono-nitration product was 95% (Found: C, 53·3; H, 4·9%), which on oxidation gave a mixture of nitrobenzoic acids (*M*, by titration, 169) in 77% yield; this on separation was found to contain: para-, m. p. 210—215° (mixed m. p. 227—229°), 68·6%; meta-, m. p. 122—125° (mixed m. p. 135—137°), 8·4%; ortho- (by difference), 23%.

(Expt. 35.) Nitration yields, 95% (Found: C, 53·9; H, 5·1%). On oxidation the nitration mixture gave acids in 71% yield, which on separation gave: para-, m. p. 236° (alone or mixed), 68%; meta-, m. p. 126—128° (mixed m. p. 138—140°), 7·0%; ortho- (by difference), 25%.

Nitration of Methyl Benzylidenemalonate.—(Expt. 21.) The yield of mononitro-product was 96% (Found: C, 53·9; H, 4·2. Calc.: C, 54·3; H, 4·2%). The whole product was oxidised with 2%

potassium permanganate and gave nitrobenzoic acids in 93% yield (*M*, by titration, 164), the bulk of the *p*-nitrobenzoic acid being allowed to crystallise out in the pure state. Separation by the usual methods gave: para-, m. p. 235° (alone or mixed), 67%; impure meta-, m. p. 104—110°, 5·8%. The meta-acid was recrystallised from a small quantity of ethyl acetate–ligroin, and a quantity corresponding to 2·4%, m. p. 122—126° (mixed m. p. 133—138°) was obtained. Hence the composition of the nitration mixture is: para-, 67%; meta-, 2·4%; ortho- (by difference), 30·6%.

A second portion of the nitration product was crystallised from absolute alcohol before oxidation, and 61% of pure methyl *p*-nitrobenzylidenemalonate, m. p. 134° (either alone or mixed with a synthetic specimen), separated out. The residue from the mother-liquor on oxidation gave nitrobenzoic acids in 96% yield (*M*, by titration, 168·5), which on separation gave a further 5·2% of *p*- and 5·3% of *m*-nitrobenzoic acid, m. p. 113—120° (both calculated on whole nitration product); the latter on recrystallisation from ethyl acetate–ligroin gave 3%, m. p. 134—136° (mixed m. p. 137—139°). Hence the composition of the nitration product was: para-, 66·6%; meta-, 3%; ortho- (by difference), 30·8%.

(Expt. 22.) The yield of mononitration product was 96% (Found: C, 54·0; H, 4·2%), which on oxidation gave nitrobenzoic acids in 84% yield (*M*, by titration, 166); these on separation gave: para-, m. p. 238°, 67·8%; meta- (after crystallisation), m. p. 134—136°, 3·3%; ortho- (by difference), 28·9%. A second portion of the nitration product was crystallised from alcohol, and 65·4% of nearly pure methyl *p*-nitrobenzylidenemalonate separated, m. p. 133—134° (mixed m. p. with a synthetic specimen, 135—136°). The residue on oxidation gave nitrobenzoic acids in 82% yield, which on separation yielded a further 2% of para-, m. p. 220—223°, and 3% of meta- (after crystallisation), m. p. 133—135° (mixed m. p. 137—139°) (both calculated on the whole nitration product). Hence the composition of the nitration product is: para-, 67·4%; meta-, 3·0%; ortho- (by difference), 29·6%.

Nitration of Methyl Atropate.—(Expt. 41.) The yield of mononitro-products was theoretical (Found: C, 57·4; H, 4·5. Calc. for $C_{10}H_9O_4N$: C, 57·9; H, 4·4%), and crystallisation from absolute methyl alcohol gave 16·3% of pure *methyl* p-*nitroatropate*, m. p. 110° (unchanged by further crystallisation). The residue from the mother-liquor on oxidation gave nitrobenzoic acids in 85% yield (*M*, 173; benzoic acid, by sublimation, 3%), which on separation were found to contain 44% of *p*-nitrobenzoic acid, m. p. 220° (mixed m. p. 221—225°), and 9% of *m*-nitrobenzoic acid. The latter, however,

was slightly sticky, and was therefore converted into its methyl ester through the acid chloride, and the residue washed with a drop of methyl alcohol on porous porcelain; the residual ester had m. p. 75—78° (mixed m. p. 78°, with a synthetic specimen of methyl *m*-nitrobenzoate). Hence the composition of the nitration product is: para-, 16·3% + (44% of 83·7%) = 53%; meta-, approx. 9% of 83·7% = approx. 7%; ortho- (by difference), 40%.

(Expt. 42.) The yield of mononitro-product was 99% (Found: C, 57·4; H, 4·7%), which was completely oxidised to the mixed nitrobenzoic acids. These, on separation, gave para-, m. p. 220—222° (alone or mixed with a genuine specimen), 57%; meta-, m. p. 110—115° (mixed m. p. 133—135°), 4·7%; ortho- (by difference), 39·3%.

Nitration of Methyl Cinnamylidenemalonate.—In a preliminary experiment, the nitration product, on being poured on ice, gave a yellow, flocculent solid, which became sticky on filtering, and on drying overnight in a vacuum desiccator over phosphoric oxide decomposed to a semi-solid gum. The whole product was therefore oxidised with potassium permanganate, but gave only a 69% yield of mixed nitrobenzoic acids. On separation, this was shown to contain less than 2% of the meta-derivative. Under the following conditions, however, it was found possible to isolate the solid nitration product.

(Expt. 12.) The nitration was carried out with nitric acid (*d* 1·46), and the product was poured on ice, *partially* neutralised with a 10% solution of sodium hydroxide, and the separated solid rapidly filtered through a Buchner funnel surrounded with ice. After being washed with ice-cold water, the solid was quickly transferred to a vacuum desiccator over phosphoric oxide, and when dry was found to be quite stable. The aqueous mother-liquor and washings were extracted with ether, the ether extract washed five times with 2*N*-sodium carbonate solution, dried over calcium chloride, and the ether evaporated at the ordinary temperature. The yield of mono-nitration product was 103% (slight dinitration) (Found: C, 56·6; H, 4·5. Calc. for $C_{14}H_{13}O_6N$: C, 57·7; H, 4·5%). After two recrystallisations from methyl alcohol, 33·3% of practically pure methyl *p*-nitrocinnamylidenemalonate, m. p. 139—143°, separated, which after crystallisation from ethyl acetate–ligroin had m. p. 146°, either alone or mixed with a synthetic specimen. The residue from the combined mother-liquors was oxidised with a boiling 2% solution of potassium permanganate, and gave nitrobenzoic acids in 78% yield (*M*, by titration, 165). On separation, this fraction gave 9·5% of *p*-nitrobenzoic acid, whilst the meta-isomeride present was less than 1·5%, since only a negligible quantity

of the meta-barium salt crystallised out, the amount present, therefore, only being represented by the solubility correction. The composition of the nitration product was thus: para-, 33·3% + (9·5% of 66·6%) = 40% ; meta-, <1%; ortho- (by difference), 59%.

Summary.

Substance nitrated.	Proportion of isomerides present, *o*-.	*m*-.	*p*-.	Mean % of *m*-.	Mean % of *p*-.
$CH_2Ph{\cdot}CH(CO_2Me)_2$	22·1	7·5	70·4		
	21·9	6·8	71·3		
	27·0	9·0	64·0	8	68
	23·0	8·4	68·6		
	25·0	7·0	68·0		
$CHPh{:}C(CO_2Me)_2$	30·6	2·4	67	3	67
	30·8	3·0	66·2		
	28·9	3·3	67·8		
	29·6	3·0	67·4		
$CPh(CO_2Me){:}CH_2$	40	approx. 7	53	5	55
	39·3	4·7	57		
$CHPh{:}CH{\cdot}CH{:}C(CO_2Me)_2$	59	<1	40	<1	40

The authors desire to express their thanks to Professor C. K. Ingold, F.R.S., for his interest and advice during the progress of this investigation, and to the Royal Society for defraying part of the expense incurred.

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CCLXXXIII.—1-*Phenyl*-4-*amino*-5-*ketopyrazoline*-3-*carboxylic Acid.*

By FREDERICK DANIEL CHATTAWAY and WILLIAM GERALD HUMPHREY.

ALTHOUGH it is well established that under the influence of acids, diketosuccinic acid phenylosazone is converted into 1-phenyl-4:5-diketopyrazoline-3-carboxylic acid 4-phenylhydrazone (I), the reduction of this compound to 1-*phenyl*-4-*amino*-5-*ketopyrazoline*-3-*carboxylic acid* (II) has never been satisfactorily effected (compare Bernthsen, *Chem.-Ztg.*, 1898, 457; Eibner and Laue, *Ber.*, 1906, **39**, 2022). If, however, reduction is effected by using the theoretical amount of sodium amalgam, and the amino-acid is liberated in the presence of some excess of sulphur dioxide (to prevent oxidation), it can be isolated in a pure condition.

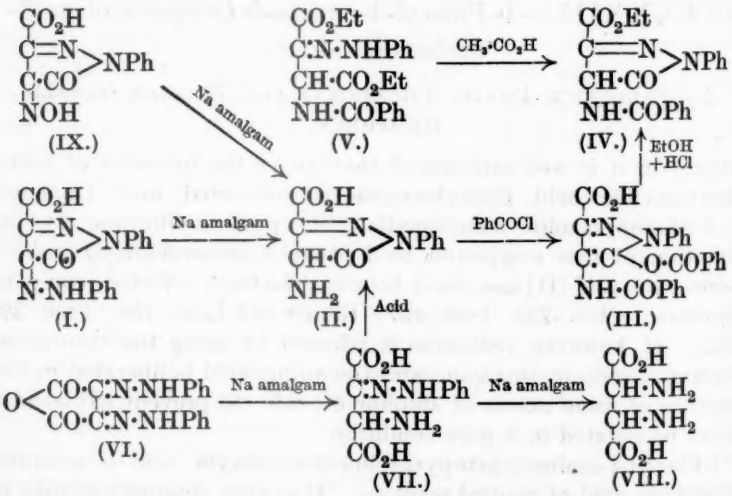
1-Phenyl-4-amino-5-ketopyrazoline-3-carboxylic acid is a white, crystalline solid of neutral reaction. It is very sparingly soluble in all ordinary organic solvents, but dissolves readily both in aqueous acids and in alkalis, such solutions oxidising rapidly in presence of

air, especially when warm. Alkaline solutions are the more readily oxidised, giving a silver mirror with ammoniacal silver oxide, and precipitating cuprous oxide from warm Fehling's solution. Acid solutions reduce ferric chloride and potassium permanganate in the cold.

It combines with 1 mol. of hydrogen chloride yielding a comparatively stable *hydrochloride*, which, however, turns violet on exposure to air. With acetic anhydride it gives a soluble, well-crystallised *acetyl* derivative of marked acid character. With benzoyl chloride it yields a *dibenzoyl* derivative, and on boiling this for a short time with alcohol containing a little hydrogen chloride, it is converted into ethyl benzoate and the ester of a monobenzoyl derivative (IV), identical with the compound obtained by Wislicenus by boiling ethyl oxalylhippurate phenylhydrazone (V) with acetic acid (*Ber.*, 1891, **24**, 1260).

1-Phenyl-4-amino-5-ketopyrazoline-3-carboxylic acid may be obtained in several other ways. For example, it is formed when the alkaline solution of amino-oxalacetic acid phenylhydrazone (VII), obtained by partial reduction of anhydrodiketosuccinic acid phenylosazone (VI) by sodium amalgam, is acidified, ring closure occurring under the influence of acids, just as in the case of diketosuccinic acid phenylosazone.

The amino-ketopyrazoline has also been prepared by reduction of the corresponding oximino-compound (IX), obtained by the action of nitrous acid on 1-phenyl-5-ketopyrazoline-3-carboxylic acid.



The action of bromine upon 1-phenyl-4 : 5-diketopyrazoline-3-carboxylic acid 4-phenylhydrazone has been re-examined and

the product shown to be 1-*phenyl*-4 : 5-*diketopyrazoline*-3-*carboxylic acid* 4-p-*bromophenylhydrazone*, since on reduction it yields *p*-bromoaniline and 1-phenyl-4-amino-5-ketopyrazoline-3-carboxylic acid. This constitution has been confirmed by its synthesis from 1-phenyl-5-ketopyrazoline-3-carboxylic acid and *p*-bromobenzenediazonium chloride.

Anhydrodiketosuccinic acid phenylosazone, like the corresponding halogenated derivatives (Chattaway and Humphrey, this vol., p. 1327), reacts with alcohols containing hydrogen chloride to give esters of the isomeric pyrazoline derivative. Several of these esters have been prepared, and it is noteworthy that the n-*propyl* and n-*butyl* esters have almost the same melting points.

EXPERIMENTAL.

Reduction of 1-*Phenyl*-4 : 5-*diketopyrazoline*-3-*carboxylic Acid* 4-*Phenylhydrazone* (I) *to* 1-*Phenyl*-4-*amino*-5-*ketopyrazoline*-3-*carboxylic Acid* (II).—17 G. of the phenylhydrazone were dissolved in 500 c.c. of a hot 1% solution of sodium hydroxide and placed in a wide-necked bottle closed by a cork, through which passed a wide glass tube reaching to the surface of the liquid and loosely stoppered at its upper end. The bottle was placed in a freezing mixture until about half of the liquid had frozen, and the air above the liquid was displaced by loosening the cork and passing a rapid stream of hydrogen down the tube. Successive small quantities of 2½% sodium amalgam were then introduced down the tube, and the mixture was vigorously shaken after each addition until the solution just became colourless and turbid due to the separation of aniline; about 250 g. of amalgam were required, and the reduction occupied 2—3 hours. The mixture was poured immediately into 800 c.c. of 2½% sulphuric acid (saturated with sulphur dioxide) and cooled to 0°. The 1-*phenyl*-4-*amino*-5-*ketopyrazoline*-3-*carboxylic acid* at once separated as a white, crystalline precipitate. It was filtered off immediately, washed thoroughly with air-free water, alcohol, and ether, and dried in a vacuum desiccator over calcium chloride; yield, 10 g.; m. p. 225° (decomp.; with darkening from 215°) (Found: C, 54·6; H, 3·9; N, 18·8. $C_{10}H_9O_3N_3$ requires C, 54·8; H, 4·1; N, 19·2%). This acid is comparatively stable when dry, but slowly oxidises and turns brownish-pink on keeping. It is very sparingly soluble in water or ether, and only sparingly soluble in boiling alcohol, benzene, chloroform, or acetone; such solutions rapidly oxidise and turn brown on exposure to air; it was therefore impossible to purify the compound by crystallisation.

The *hydrochloride* separates on cooling a hot saturated solution of the amino-ketopyrazoline in concentrated hydrochloric acid.

It forms long, colourless prisms which begin to darken and decompose at 160°; it is fairly stable when dry, but its aqueous solution darkens on keeping and the crystals themselves slowly become pale violet (Found : C, 13·7. $C_{10}H_{10}O_3N_3Cl$ requires Cl, 13·9%).

Acetyl derivative. 1-Phenyl-4-amino-5-ketopyrazoline-3-carboxylic acid dissolves apparently unchanged in boiling acetic anhydride, the solution rapidly turning dark reddish-brown owing to oxidation. On adding a drop of concentrated sulphuric acid, a vigorous reaction occurs; on adding a few drops of water and cooling, the *acetyl* compound crystallises out. It is easily soluble in hot acetic acid, from which it separates in long, colourless prisms, m. p. 216° (Found : C, 55·0; H, 4·2; N, 16·0. $C_{12}H_{11}O_4N_3$ requires C, 55·2; H, 4·2; N, 16·1%).

Dibenzoyl derivative (III). When an alkaline solution of 1-phenyl-4-amino-5-ketopyrazoline-3-carboxylic acid is shaken with excess of benzoyl chloride, it is converted into a *dibenzoyl* derivative. The same compound is more readily prepared by heating the amine (2 g.) with benzoyl chloride (3 c.c.) until hydrochloric acid is no longer evolved, cooling, and adding ether. It was recrystallised from boiling acetic acid, in which it is easily soluble and from which it separates in long, colourless prisms, m. p. 205° (Found : C, 67·7; H, 3·9; N, 10·0. $C_{24}H_{17}O_5N_3$ requires C, 67·5; H, 4·0; N, 9·8%).

Ethyl ester of 1-*phenyl*-4-*benzamido*-5-*ketopyrazoline*-3-*carboxylic acid* (IV). When the dibenzoyl derivative (III) is boiled for a short time with alcohol containing 1% of hydrogen chloride, an ethyl group is introduced and one benzoyl group removed. The bright yellow solution thus obtained smells strongly of ethyl benzoate, and on cooling, the *ethyl* ester separates in long, slender, canary-yellow prisms, m. p. 195° (Found : N, 12·1. $C_{19}H_{17}O_4N_3$ requires N, 12·0%).

Preparation of 1-*Phenyl*-4-*amino*-5-*ketopyrazoline*-3-*carboxylic Acid by Reduction of Anhydrodiketosuccinic Acid Phenylosazone.*—The reduction of anhydrodiketosuccinic acid phenylosazone proceeds in two stages. The reduction by alkaline reducing agents of one phenylhydrazone group must first give amino-oxalacetic acid phenylhydrazone; this, however, cannot be isolated, for on acidification ring closure and pyrazoline formation occur and 1-phenyl-4-amino-5-ketopyrazoline-3-carboxylic acid is produced. This change was to be expected, since the disodium salt of the osazone is itself converted quantitatively into a pyrazoline derivative on acidification.

The reduction of both phenylhydrazone groups by alkaline reducing agents yields the two stereoisomeric diaminosuccinic acids, which separate when the solution is acidified. These compounds

were prepared by Farchy and Tafel by reduction of the osazone (*Ber.*, 1893, **26**, 1980).

Partial reduction. A fine suspension of 17 g. of anhydrodiketosuccinic acid phenylosazone in 500 c.c. of 1% sodium hydroxide solution was cooled in a freezing-mixture and treated with successive small quantities of 2½% sodium amalgam in the apparatus described above, until the yellow colour had just disappeared; about 250 g. of the amalgam were required. The colourless liquid was then decanted from the remaining mercury and slowly poured into 800 c.c. of ice-cold 2½% sulphuric acid saturated with sulphur dioxide; 1-phenyl-4-amino-5-ketopyrazoline-3-carboxylic acid then separated as a white precipitate which was filtered off, washed, and dried as before; yield, 9 g. It was shown to be identical with the compound previously described, since it melted at 215—225° with complete decomposition, and yielded an identical acetyl derivative, m. p. 216°.

Complete reduction. A fine suspension of 19 g. of the anhydride in 500 c.c. of a 1% aqueous solution of sodium hydroxide was cooled and reduced with a considerable excess of 2½% sodium amalgam (650 g.) in the manner described by Farchy and Tafel for the corresponding osazone. From the alkaline solution thus obtained, the two stereoisomeric diaminosuccinic acids were isolated and purified in precisely the same manner as described by Farchy and Tafel. The two isomerides were identified by conversion to their dibenzoyl derivatives; the dibenzoyl derivative of the *meso*-modification melts with decomp. at 213°, and that of the *r*-acid at 183°.

1-*Phenyl*-4-*oximino*-5-*ketopyrazoline*-3-*carboxylic Acid* (IX).—10 G. of 1-phenyl-5-ketopyrazoline-3-carboxylic acid (prepared from ethyl oxalacetate phenylhydrazone, as described by Wislicenus, *Annalen*, 1888, **246**, 319) and 5 g. of sodium nitrite were dissolved in 150 c.c. of 30% aqueous potassium hydroxide; the solution was cooled to 0° and added slowly to 200 c.c. of 10% hydrochloric acid. The *oximino*-compound separated as a red precipitate, which after 12 hours was filtered off and crystallised from acetic acid, in which it is easily soluble, and from which it separates in glittering, red, slender prisms, m. p. 209° (decomp.); yield, 9 g. (Found: N, 17·8. $C_{10}H_7O_4N_3$ requires N, 18·0%).

When reduced it yields 1-phenyl-4-amino-5-ketopyrazoline-3-carboxylic acid. A solution of 2 g. of the oximino-compound in 100 c.c. of a 1% aqueous solution of sodium hydroxide was cooled in a freezing mixture and reduced with 40 g. of 2½% sodium amalgam. The colourless solution was then poured into 120 c.c. of 3% sulphuric acid, saturated with sulphur dioxide. The amino-keto-

pyrazoline separated as a white, crystalline powder, which was filtered off, washed, and dried as before. Yield 1·7 g. It was identified by its acetyl derivative, m. p. 216°.

Bromination of 1-*Phenyl*-4 : 5-*diketopyrazoline*-3-*carboxylic Acid* 4-*Phenylhydrazone*.—In view of recent work on the bromination of phenylhydrazones (J., 1925, **127**, 975, 1687, 2407; this vol., p. 1323), it was of interest to determine to what extent bromine would enter the phenylhydrazone residue in 1-phenyl-4 : 5-diketopyrazoline-3-carboxylic acid 4-phenylhydrazone. 6 G. (1 mol.) of the hydrazone were suspended in 400 c.c. of glacial acetic acid containing 4 c.c. (4 mols.) of bromine, and boiled for 8 hours. Hydrogen bromide was evolved, and on cooling, the *bromination product* separated as a yellow solid. It was crystallised from boiling acetic acid, in which it is sparingly soluble, and from which it separates in short, yellow prisms, m. p. 258° (decomp.). Yield, 6 g. (Found : Br, 20·6. $C_{16}H_{11}O_3N_4Br$ requires Br, 20·7%).

The bromine was shown to have entered the para-position by the production of *p*-bromoaniline on reduction : 5 G. of the bromination product were dissolved in 150 c.c. of 1% aqueous sodium hydroxide and reduced as before with 80 g. of 2½% sodium amalgam; when this was poured into 200 c.c. of 2½% sulphuric acid, saturated with sulphur dioxide, 1-phenyl-4-amino-5-ketopyrazoline-3-carboxylic acid separated as a white precipitate (yield, 2 g.; acetyl derivative, m. p. 216°). The acid filtrate was concentrated, made alkaline with caustic soda and steam-distilled. *p*-Bromoaniline (m. p. 63°) distilled over, and was identified by conversion to its acetyl derivative, m. p. 167°.

The constitution of the bromination product was further established by its synthesis from 1-phenyl-5-ketopyrazoline-3-carboxylic acid by the action of *p*-bromobenzenediazonium chloride. 2 G. of *p*-bromoaniline were suspended in 3·5 c.c. of concentrated hydrochloric acid and diazotised with 1 g. of sodium nitrite in 25 c.c. of water; the small excess of nitrous acid was removed by bubbling air through the solution, which was then added to a solution of 2 g. of 1-phenyl-5-ketopyrazoline-3-carboxylic acid in 100 c.c. of a 2% aqueous solution of potassium hydroxide. 1-Phenyl-4 : 5-diketopyrazoline-3-carboxylic acid 4-*p*-bromophenylhydrazone separated as a yellow precipitate, which, after the addition of excess of hydrochloric acid, was filtered off, washed with hot alcohol, and crystallised from acetic acid. It melted at 258° (decomp.) and was identical in all respects with the compound obtained by the direct bromination (above).

In the course of this investigation, several esters of 1-phenyl-4 : 5-diketopyrazoline-3-carboxylic acid 4-phenylhydrazone have

been prepared by the action of alcohols containing hydrogen chloride on anhydrodiketosuccinic acid phenylosazone. The *methyl* ester, obtained by boiling the phenylosazone (2 g.) for 24 hours with methyl alcohol (30 g.) saturated with dry hydrogen chloride, crystallises from alcohol, in which it is easily soluble, in fine, yellow needles, m. p. 138° (Found: N, 17·4. $C_{17}H_{14}O_3N_4$ requires N, 17·4%). The ethyl ester (Wislicenus and Scheidt, *Ber.*, 1891, **24**, 4210), m. p. 153°, is obtained in a similar manner. The n-*propyl* ester crystallises from acetic acid, in which it is easily soluble, in long, deep yellow prisms, m. p. 116·5° (Found: C, 65·0; H, 4·9; N, 16·1. $C_{19}H_{18}O_3N_4$ requires C, 65·1; H, 5·1; N, 16·0%). The n-*butyl* ester crystallises from acetic acid in long prisms, not quite so deep in colour as those of the *n*-propyl ester but melting at practically the same temperature, 117° (a mixture of these two esters had m. p. 112°) (Found: C, 66·2; H, 5·5; N, 15·5. $C_{20}H_{20}O_3N_4$ requires C, 65·9; H, 5·5; N, 15·4%).

THE QUEEN'S COLLEGE, OXFORD. [*Received, June 29th*, 1927.]

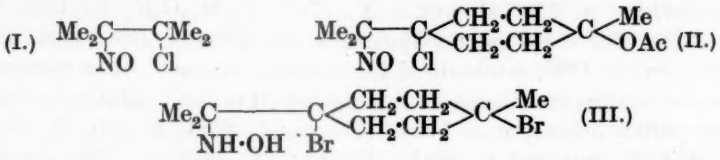
CCLXXXIV.—*The Action of Hydrogen Iodide on Nitroso-compounds.*

By JOHN CAMPBELL EARL and JAMES KENNER.

THE observation of the ortho-para directive influence of the nitroso-group in aromatic substitution was considered by Ingold (J., 1925, **127**, 513) to be in conflict with the theory of induced alternate polarity, but a theoretical discussion of the nitroso-group by Robinson (*Chem. and Industry*, 1925, **44**, 456) showed this to be at least not necessarily the case. In addition, it was pointed out (Kenner, Tod, and Witham, J., 1925, **127**, 2343) that, quite apart from any purely theoretical considerations, the well-known liberation of iodine from hydrogen iodide by nitrous acid, by hypochlorous acid, and by hydrogen peroxide is a simple experimental indication of possible similarity in polar properties of the nitroso-group, the chlorine atom, and the hydroxyl group. The analogy is not perfect, since in the case of nitrous acid the primary nitrogenous product undergoes a further reaction with formation of nitric oxide, but a parallelism also exists between the behaviours of the nitroso-group and chlorine, in that each is readily displaced from *N*-nitroso- or -chloro-amines and -acetanilides (von Pechmann and Frobenius, *Ber.*, 1894, **27**, 651).

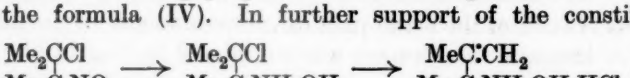
It seemed that further evidence in regard to the nature of the nitroso-group might be obtained from a study of the action of

hydrogen iodide on nitroso-compounds in general. Reference to the literature showed that among aliphatic compounds, iodine is liberated from hydrogen iodide by the nitrosochlorides of tetramethylethylene (I) (Thiele, *Ber.*, 1894, **27**, 456) and $\Delta^{4(8)}$-menthen-1-ol (γ-terpineol) acetate (II) (Baeyer, *ibid.*, p. 446). Later, Baeyer showed the



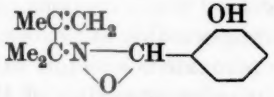
(I.) (II.) (III.)

nitrosobromide of 1-bromo-$\Delta^{4(8)}$-menthene to be converted into the hydroxylamino-derivative (III) by hydrogen bromide, in the presence of red phosphorus as an absorbent of the bromine liberated, and concluded that the reaction with hydrogen iodide follows a similar course. Baeyer observed (*loc. cit.*) that the nitrosochlorides of tetramethylethylene and menthenol acetate behaved differently towards hydrogen bromide in acetic acid. There is, however, no essential difference between the two reactions. The product derived from tetramethylethylene nitrosochloride is a basic substance, which, like the compounds examined by Baeyer, loses the elements of hydrogen chloride when it is liberated in the presence of alkali. The colourless *hydrochloride* of the resulting unsaturated base exhibits reducing properties and its composition corresponds with the formula (IV). In further support of the constitution



(IV.)

assigned to this compound, it was shown to furnish a *condensation product* with salicylic aldehyde, the composition of which was in accord with the formula (V) (compare Bamberger, *Ber.*, 1894, **27**, 2556).



(V.)

There seemed also a possibility that the negative character of the nitroso-group might induce positive polarity in the chlorine atom, which, in the presence of hydrogen iodide, would render it liable to displacement by hydrogen. It was, however, shown that this does not occur in either of the above instances, since the quantity of iodine liberated in the reaction was found to correspond approximately with the decrease in the amount of halogen ion present in solution. The slight discrepancy was shown to be attributable to formation of chlorine ions by hydrolytic action, which

occurred in absence of hydrogen iodide under otherwise similar experimental conditions.

Since the conditions for the transmission of the influence of the nitroso-group to the chlorine atom should be more favourable in the aromatic nucleus than in the above compounds, the behaviour of *p*-chloronitrosobenzene towards hydrogen iodide was investigated. Here also reduction occurred, being immediately followed by condensation of the hydroxylamine with the nitroso-derivative, so that 4 : 4′-dichloroazoxybenzene was produced in excellent yield. No elimination of halogen occurred from *p*-chloronitrosobenzene or from its meta-isomeride under the conditions employed. The nitroso-group itself is therefore the sole point of attack by hydrogen iodide in such cases. Doubtless its reactivity in the aromatic compounds is affected by the position of the chlorine atom, but our hopes of demonstrating this relationship could not be realised owing to the uncertainty as to the relative proportions of polymerised and unpolymerised material present in solution, and to the condensation of nitroso- with hydroxylamino-derivatives just mentioned.

In order further to demonstrate the general character of the reaction here discussed, δ-nitroso-δ-methylpentan-β-one (VI) (Harries, *Ber.*, 1898, **31**, 1379), 8-nitrosomenthone (VII) (Harries and Rolder, *Ber.*, 1899, **32**, 3365), and 4-nitrosomenthone (VIII) (Baeyer, *Ber.*, 1894, **27**, 1912; 1895, **28**, 1586) were examined qualitatively in respect of their behaviour towards hydrogen iodide.

(VI.) $CMe_2(NO)\cdot CH_2\cdot COMe$ $\qquad$ $Me_2C(NO)\cdot CH<\begin{matrix}CH_2\cdot CH_2\\CO-CH_2\end{matrix}>CHMe$ (VII.)

$Me_2CH\cdot C(NO)<\begin{matrix}CH_2\cdot CH_2\\CO-CH_2\end{matrix}>CHMe$ (VIII.)

In each case, iodine was liberated, but the rate of reaction, as in other cases, was affected by the degree of polymerisation of the nitroso-compounds.

It may therefore be concluded that nitroso-compounds, in general, are reduced by hydrogen iodide to the corresponding hydroxylamines. The facility with which this occurs is in remarkable contrast to the behaviour of carbonyl compounds, with which nitroso-compounds are in some respects comparable. The significance of this contrast will be dealt with in a subsequent paper discussing the chemistry of nitroso-compounds. Meanwhile, the possibility must be entertained in the case of nitrous acid, also, that

$HO\cdot NO \longrightarrow HO\cdot NH\cdot OH$ (IX.) $\qquad$ $H\cdot NO$ (X.)

the primary action leads to the formation of dihydroxyammonia (IX) rather than of nitroxyl (X), as might be anticipated from the

analogy between the nitroso- and hydroxyl groups or the chlorine atom mentioned at the outset of this paper. This possibility must also be regarded as the more probable, when it is recalled that the ultimate nitrogenous product of the reaction is nitric oxide, the formation of which could be represented by the equation $NH(OH)_2 + HO{\cdot}NO \longrightarrow 2NO + 2H_2O$ (compare Raschig, " Schwefel und Stickstoffstudien," Leipzig, 1925, p. 19; Angeli and Angelico, *Gazzetta*, 1900, **30**, i, 593; *Ber.*, 1904, **37**, 2390).

Experimental.

Reduction of Tetramethylethylene Nitrosochloride by Hydrogen Bromide.—A concentrated glacial acetic acid solution of hydrogen bromide (42 c.c.) was mixed with red phosphorus (1·4 g.) and cooled in ice-water until crystallisation commenced (12°); tetramethylethylene nitrosochloride (7 g.) was then added with thorough stirring. The reaction was completed by passing a stream of hydrogen bromide into the ice-cooled mixture during a period of 1 hour, and stirring for another 2 hours. The liquid was then added to a mixture of ice (60 g.) and water (60 g.), and the undissolved material filtered off. Benzene (50 c.c.) was added, together with sufficient sodium hydroxide solution to render the aqueous layer strongly alkaline. The liberated base passed into solution in the benzene, and after further extraction of the alkaline solution with benzene, the united extracts were shaken four times with hydrochloric acid (25 c.c.) diluted with an equal volume of water. The solid residue obtained by evaporating the united acid extracts to dryness under reduced pressure was purified by filtering its solution in alcohol, and again evaporating to dryness. The *hydrochloride* of *β-hydroxylamino-βγ-dimethyl-Δ$^{\gamma}$-butene* so obtained (4·5 g.) was further purified by recrystallisation from alcohol (Found: N, 9·5; Cl, 23·1. $C_6H_{13}ON,HCl$ requires N, 9·2; Cl, 23·2%). The base reduced Fehling's solution in the cold.

When the hydrochloride (0·8 g.) was dissolved in water (5 c.c.) with the addition of crystalline sodium acetate (1·2 g.), salicylic aldehyde (0·65 g.), and alcohol (5 c.c.), condensation readily occurred at the ordinary temperature. After 19 hours, the mixture was poured into ice water, and an oil separated which soon crystallised. The solid (0·55 g.) was filtered off, and a further quantity (0·2 g.) separated on saturating the filtrate with salt and cooling in ice. After one crystallisation from alcohol, the *condensation product* melted sharply at 53° (Found, by micro-analysis: N, 6·4. $C_{13}H_{17}O_2N$ requires N, 6·4%).

Reduction of Tetramethylethylene Nitrosochloride by Hydrogen Iodide.—A solution of the nitrosochloride (0·1355 g.) in pure benzene

(10 c.c.) was shaken with a mixture of an approximately $N/5$-solution of potassium iodide (corresponding to 19·94 c.c. of accurately $N/5$-solution) and an approximately $N/2$-solution of sulphuric acid (20 c.c.). After 3½ hours, the benzene layer, which contained the bulk of the liberated iodine, was separated, and the aqueous layer extracted with benzene until practically colourless. The halogen ion in the aqueous solution was then titrated with silver nitrate and potassium thiocyanate in the usual way, and found equivalent to 13·12 c.c. of $N/5$-solution. The united benzene solutions were shaken with excess of standard sodium thiosulphate, the excess being titrated with standard iodine. The iodine thus determined corresponded to 7·43 c.c. of $N/5$-solution.

It would thus appear that halogen corresponding to 0·61 c.c. of $N/5$-solution had been furnished by elimination of chlorine from the nitrosochloride. This occurred by hydrolysis, for when a similar benzene solution of the nitrosochloride was shaken for 3½ hours with dilute sulphuric acid under very similar conditions, the aqueous layer contained halogen corresponding to 2·0 c.c. of $N/5$-solution. In this case, of course, there was no decrease in the concentration of the nitrosochloride solution owing to reduction during the experiment, so that the amount of hydrolysis is higher than in the reduction experiments.

Reduction of γ-Terpinyl Acetate Nitrosochloride by Hydrogen Iodide.—The reaction was slower than in the case of the tetramethylethylene derivative so that a higher concentration of the nitrosochloride (0·2466 g. in 10 c.c. of benzene) was employed, and the shaking was continued for 5 hours. In other respects, the experimental conditions were similar to those described above.

Halogen originally present in aqueous solution = 19·94 c.c.
„ finally „ „ „ „ = 18·75 c.c.
Iodine liberated = 1·37 c.c.

Here, again, there is evidence of slight hydrolysis.

Reduction of Chloronitrosobenzenes by Hydrogen Iodide.—Both the *m*- and *p*-isomerides were examined in the usual way, 0·5 g. of the substance in benzene (10 c.c.) being used, and the shaking being continued for 4 hours.

	m-.	*p*-.
Halogen originally present in aqueous solution (c.c. of $N/5$)	19·94	19·94
„ finally „ „ „ „	17·82	18·72
Iodine liberated (c.c. of $N/5$)	2·08	1·57

These results indicate a similarity in behaviour to the two nitrosochlorides, but in neither case was there any evidence of the removal of chlorine by hydrolysis.

An attempt was made to modify the reduction in such a way that

the isolation of the reduction products would be possible. For this purpose, it was necessary to introduce some substance to remove the iodine as formed. Red phosphorus, mercury, and sodium thiosulphate were all successfully employed. Thus a mixture of *p*-chloronitrosobenzene (1 g.) red phosphorus (1 g.), and glacial acetic acid (25 c.c.) was well stirred at room temperature, and hydriodic acid (*d* 1·7; 5 c.c.) added drop by drop during 5 minutes. The mixture became warm and a mass of crystalline material separated. After a further 5 minutes, water was added, and the precipitated material was filtered off and washed thoroughly with water. The *pp'*-dichloroazoxybenzene was extracted from the residue by repeated maceration with ether, and the solvent allowed to evaporate at room temperature. The product so obtained (0·83 g.) melted at 153—154°, and at 154° after one recrystallisation from alcohol (Found, by micro-analysis: N, 10·7. Calc. for $C_{12}H_8ON_2Cl_2$: N, 10·5%). In another experiment the azoxy-compound (0·7 g., m. p. 153°) was obtained from the nitroso-derivative (0·85 g.), glacial acetic acid (25 c.c.), mercury (9·5 g.), and hydriodic acid (*d* 1·7; 3 c.c.).

From *m*-chloronitrosobenzene by means of phosphorus, *mm'*-dichloroazoxybenzene, m. p. 96°, was obtained (Found: N, 10·1%).

Action of Hydriodic Acid on the Nitroso-derivatives.—δ-Nitroso-δ-methylpentan-β-one yielded a colourless solution in acetone, which only reacted very slowly at the ordinary temperature with hydriodic acid, but when the solution was first warmed until a definite blue colour had developed, and then cooled, liberation of iodine occurred much more rapidly. 8-Nitrosomenthone, though blue when first prepared, slowly polymerises and therefore also reacts comparatively slowly with hydriodic acid in acetone solution. 4-Nitrosomenthone was definitely recognised by Baeyer (*loc. cit.*) to be a bis-compound, but nevertheless has some tendency towards dissociation since its solution in xylene became blue when heated. Although no similar development of colour occurred in boiling acetone solution, yet iodine was slowly liberated when a cold solution in acetone was treated with hydriodic acid.

Note on the Action of Hydriodic Acid on Ether.—Whilst it is well known that hydrogen iodide reacts with ethyl ether to form ethyl iodide, it is not recorded in the standard work of reference that they react in some way at the ordinary temperature with formation of iodine. This was observed in connexion with the experiments now described, and prevented the use of ether as solvent in cases where it would otherwise have been very desirable. The only reference to this reaction which we have been able to find is a statement by Hantzsch, who experienced the same difficulty and stated

that "Jodwasserstoff in diesem Medium schon durch unvermeidliche Spuren von Sauerstoff zum Trijodwasserstoff oxydiert wird" (*Z. Elektrochem.*, 1923, **29**, 232). In a quantitative experiment with ether purified in the usual manner (20 c.c.), aqueous potassium iodide solution (*N*/5, 20 c.c.), and dilute sulphuric acid (*N*/2, 20 c.c.), the iodine liberated after some days at the ordinary temperature required 8·5 c.c. of *N*/10-thiosulphate.

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CCLXXXV. — *Co-ordination Compounds of Quinquevalent Molybdenum.*

By ROBERT GILBERT JAMES and WILLIAM WARDLAW.

ONE important result of the application of electronic theories of valency to co-ordination compounds has been to indicate the relative stabilities of the systems within the co-ordination sphere. The marked stability of the ion $Mo(CN)_8''''$, present in an aqueous solution of the complex salt $K_4Mo(CN)_8$, can be readily appreciated when it is seen that the effective atomic number of the molybdenum is 54—that of the next inert gas—and that the associating units are regularly distributed. The stability of complex salts is not, however, the same for all associated units, the order of decreasing stability being cyanides, fluorides, thiocyanates, chlorides, bromides, and iodides, and this third factor must always have consideration. In a recent investigation (this vol., p. 512) on the complex chlorides of tervalent molybdenum, such as K_3MoCl_6 and K_2MoCl_5,H_2O, it was shown that ionisation in dilute aqueous solution produced initially four and three ions, respectively, but that the complex ions were gradually decomposed. Here, the effective atomic number of the metallic atom is 51 and the decreased stability of the complex ion $MoCl_6'''$, compared with that of the ion $Mo(CN)_8''''$, is due primarily to the smaller number of electrons associated with the molybdenum atom, but also to the replacement of the cyanide by the chloride radical. With the chlorides of quinquevalent molybdenum of the general formula $R_2[MoOCl_5]$, the effective atomic number of the central atom has fallen to 49, and this is reflected in the marked changes which occur when these green, crystalline substances are dissolved in water. They give, immediately, brown solutions with acid reactions, from which it is impossible to obtain the original salt satisfactorily by crystallisation. Although these facts are well known, no systematic examination of this decomposition has hitherto been attempted. In the present research,

this has been done, and not only has it yielded information as to the course of the reaction in aqueous solution, but it has resulted in the evolution of improved methods of preparation for the complex salts themselves, and in the isolation of new series of co-ordination compounds characteristic of the intermediate stages of the hydrolytic decomposition.

EXPERIMENTAL.

Chilesotti (*Z. Elektrochem.*, 1906, **12**, 173) first showed that by electrolytic reduction of molybdenum trioxide, dissolved in hydrochloric acid of appropriate concentration, a solution containing quinquevalent molybdenum could be obtained if a platinised platinum cathode was used, whereas with a cathode of polished platinum, reduction to the tervalent state resulted. This observation has been utilised in the following preparations.

Molybdenum trioxide solution. Molybdenum trioxide (100 g.) was heated with 500 c.c. of hydrochloric acid (*d* 1·16) till dissolved; the solution was evaporated to 250 c.c., filtered, and made up to 500 c.c. with hydrochloric acid, and thus contained molybdenum trioxide (20%) in 9*N*-hydrochloric acid.

Salts of the Type $R_2[MoOCl_5]$.

Diammonium Molybdenyl Pentachloride.—Klason (*Ber.*, 1901, **34**, 148) and Nordenskjold (*ibid.*, p. 1572) obtained this salt by reducing ammonium molybdate in concentrated hydrochloric acid with hydrogen iodide, whilst Foerster and Fricke (*Z. angew. Chem.*, 1923, **36**, 458), using Chilesotti's results (*loc. cit.*), prepared it by the electrolytic reduction method, of which the following is a variation: 75 C.c. of the molybdenum trioxide solution, diluted with an equal volume of water, were placed in the cathode chamber of a diaphragm cell, of which the anode chamber contained hydrochloric acid (5*N*). A polished platinum electrode served as the anode, whilst the cathode was of platinised platinum, 5 cm. square. A current of 2·5 amp. was employed, and on electrolytic reduction to the quinquevalent stage, a reddish-brown cathode solution was obtained. This was concentrated to 50 c.c. under diminished pressure, 30 c.c. of ammonium chloride solution (containing 9 g.) were admitted, and the mixture was heated for about a minute. On saturating with hydrogen chloride and cooling, emerald-green crystals separated. These were recrystallised by dissolving in the minimum volume of water at *ca.* 80°, and saturating with hydrogen chloride until cold. The crystals were washed with concentrated hydrochloric acid and dried in a vacuum over solid potassium hydroxide.

Analysis. The molybdenum was precipitated as sulphide (J., 1924, **125**, 1911), ignited, and weighed as the trioxide, the chloride

in the filtrate and washings being estimated as silver chloride. The ammonia was determined by the distillation method, the ammoniacal distillate being titrated continuously against standard acid with bromophenol-blue as indicator [Found: Mo, 29·5; Cl, 54·4; NH_4, 11·1. Calc. for $(NH_4)_2MoOCl_5$: Mo, 29·5; Cl, 54·5; NH_4, 11·1%].

A New Electrolytic Method.—150 C.c. of the prepared molybdenum trioxide solution were placed in the cathode chamber of the diaphragm cell, the anode chamber containing ammonia (10*N*) and a small quantity of ammonium chloride. On electrolysis with a current density of 0·1 amp. per sq. cm. and continuous saturation of the cathode liquid with hydrogen chloride, the diammonium molybdenyl pentachloride separated in good yield. After being washed and dried, the crystals gave Mo, 29·3; Cl, 54·6; NH_4, 11·1%.

Dirubidium Molybdenyl Pentachloride.—This salt was first prepared by Nordenskjold (*loc. cit.*) and later by Foerster and Fricke (*loc. cit.*). By the use of the first of the methods here described for the preparation of the ammonium salt, but adding 30 c.c. of a rubidium chloride solution (containing 14 g.), yellowish-green crystals were obtained, which were washed, dried, and recrystallised (Found: Mo, 20·9; Cl, 38·6; Rb, 36·9. Calc. for Rb_2MoOCl_5: Mo, 20·9; Cl, 38·5; Rb, 37·1%).

Dipotassium Molybdenyl Pentachloride.—The methods described by Nordenskjold and by Foerster and Fricke for the preparation of this salt were found always to give a product contaminated with potassium chloride. The following method gave an excellent yield of pure salt, which, being crystallised at a high temperature, was obtained free from the more soluble alkali chloride: 75 C.c. of molybdenum trioxide solution, diluted with 75 c.c. of water, were electrolytically reduced to the quinquevalent condition. The resulting solution was concentrated under diminished pressure to 50 c.c., 30 c.c. of potassium chloride solution (containing 6·5 g.) were added, and the solution was further concentrated to 70 c.c. The flask was now placed in a thermostat at 90°, and the solution saturated with hydrogen chloride. With the hydrogen chloride still passing through the solution, the temperature was lowered to 70°, whereupon the required green salt began to separate; the temperature of the thermostat was then altered to and maintained at 60° and a high yield of the complex salt was thus obtained. The dark green crystals were filtered through a hot filter, drained in a current of dry hydrogen chloride, and dried in a vacuum over solid potassium hydroxide and phosphoric oxide [Found: Mo, 25·8; Cl, 47·4; K, 20·9. Calc. for K_2MoOCl_5: Mo, 26·1; Cl, 48·2;

K, 21·3%; the presence of a small amount of water of crystallisation ($0{\cdot}25H_2O$) accounts for the slight difference].

Dipyridinium Molybdenyl Pentachloride.—The only method previously described for the preparation of this salt is that of Rosenheim and Koss (*Z. anorg. Chem.*, **1906, 49**, 148) and of Sand and Burger (*Ber.*, 1906, **39**, 1761), who obtained it by the action of hydrochloric acid on the complex compound $Mo(OH)_2(CNS)_3(C_5H_5N)_2$. The following method gave an almost theoretical yield of pure salt: 150 C.c. of the molybdenum trioxide solution, reduced electrolytically to the quinquevalent stage, were evaporated on a water-bath under diminished pressure almost to dryness; alcohol, saturated with hydrogen chloride, was now admitted, and after warming and agitation, the reddish-brown mass dissolved producing an emerald-green solution (100 c.c.). This was cooled to room temperature, saturated with hydrogen chloride, and filtered if necessary; one half of the filtrate was utilised for the preparation of the pyridinium salt, and the other half for the quinolinium derivative. By the addition of alcohol saturated with hydrogen chloride, the 50 c.c. of solution were made up to 100 c.c., and to this water-cooled solution pyridine was added, drop by drop, with constant stirring till no more green precipitate separated (excess of pyridine gives a red solution). This was filtered and dissolved in alcoholic hydrogen chloride (2 vols. of alcohol, saturated with hydrogen chloride at room temperature, and 1 vol. of absolute alcohol). On concentrating this solution, yellowish-green crystals separated; these were filtered, washed with alcohol saturated with hydrogen chloride, and dried over potassium hydroxide and phosphoric oxide in a vacuum [Found: Mo, 21·4; Cl, 39·6; N, 6·2; C, 26·8; H, 2·7. Calc. for $(C_5H_6N)_2MoOCl_5$: Mo, 21·4; Cl, 39·5; N, 6·2; C, 26·7; H, 2·7%].

Diquinolinium molybdenyl pentachloride was prepared by adding pure quinoline (18 g.) with constant stirring to the boiling molybdenum solution previously mentioned. On evaporation and crystallisation, a large amount of the required substance was obtained, which was recrystallised and dried as in the case of the pyridinium compound [Found: Mo, 16·9; Cl, 31·2; N, 5·0; C, 37·8; H, 3·3. $(C_9H_8N)_2MoOCl_5,H_2O$ requires Mo, 16·9; Cl, 31·3; N, 4·9; C, 38·1; H, 3·2%].

Ditrimethylammonium Molybdenyl Pentachloride.—Nordenskjold (*loc. cit.*) prepared this salt by employing hydrogen iodide as a reducing agent. Using the electrolytic reduction method under conditions to be described later, the present authors isolated the first chloride of the type $R[MoOCl_4,H_2O]$ as *mono*trimethylammonium molybdenyl tetrachloride, $NMe_3H[MoOCl_4,H_2O]$ (see below), and converted it into the ditrimethylammonium pentachloride by

dissolving it in alcoholic hydrogen chloride, evaporating to small bulk, saturating with hydrogen chloride, and allowing to crystallise. After recrystallisation, the light emerald-green crystals were washed with alcoholic hydrogen chloride and dried in a vacuum over solid potassium hydroxide and phosphoric oxide {Found: Mo, 23·5; Cl, 43·2; N, 6·9; C, 17·6; H, 5·1. Calc. for $[(CH_3)_3NH]_2MoOCl_5$: Mo, 23·5; Cl, 43·3; N, 6·8; C, 17·6; H, 4·9%}.

General Properties of the Complex Salts.—The salts described in this paper generally crystallise in the rhombic form and range in colour from dark green through shades of emerald-green to yellowish-green. The pyridinium salt exhibits a strong pleochroism and has a very high double refraction. When exposed to a moist atmosphere, these salts more or less rapidly turn reddish-brown, in which condition they are very susceptible to aërial oxidation, molybdenum blue being formed. The pyridinium and the ditrimethylammonium salts give a bright copper-red substance at one stage of these changes. The potassium and the substituted-ammonium salts are the most sensitive, and the quinolinium the least sensitive, to the action of moist air. All the complex salts are soluble in water, the concentrated solutions being reddish-brown, passing through orange to bright yellow on dilution. On saturation with hydrogen chloride, these aqueous solutions finally turn emerald-green and from sufficiently concentrated solutions the complex salts separate. Alcohol dissolves all these green salts, and from the solution of the alkali complex salts, alkali chlorides separate on heating. The pyridinium salt under these conditions yields a red precipitate which will be referred to in detail later. The addition of pyridine or quinoline to aqueous solutions of any of the complex salts gives a brown, insoluble precipitate.

Physico-chemical Measurements.

Molecular-weight Determinations.—The molecular weight was determined by the depression of the freezing point of air-free water.

The figures given on p. 2150 indicate that the complex salts $R_2[MoOCl_5]$ undergo extensive ionisation in aqueous solution, and instead of yielding the (theoretical) 3 ions, furnish 9 ions in the reddish-brown solutions of concentrations *ca.* 0·02—0·05 g.-mol. per litre, and 10—11 ions in the bright yellow solutions obtained by further dilution. Additional evidence for this ionisation in aqueous solution is afforded by determinations of molecular conductivity. Table II gives the value of μ at 0° for various dilutions v (as litres per mol.).

A satisfactory explanation of the high molecular conductivity and the exceptional osmotic factor is forthcoming if it be assumed

TABLE I.

G. of substance per 100 g. of water.	Conc. (mol. per 1000 g. water).	Osmotic factor.	Apparent mol. wt.
Diammonium molybdenyl pentachloride.			
1·675	0·0515	9·00	36·15
0·725	0·0223	9·03	36·02
0·278	0·0085	10·1	32·21
M for $(NH_4)_2MoOCl_5$ = 325·3.			
Dipotassium molybdenyl pentachloride.			
2·308	0·0628	8·89	41·34
0·765	0·0208	9·12	40·30
0·285	0·0077	10·1	36·39
M for K_2MoOCl_5 = 367·5.			
Dirubidium molybdenyl pentachloride.			
1·567	0·0340	8·88	51·82
0·853	0·0185	9·11	50·52
0·457	0·0099	9·42	48·85
M for Rb_2MoOCl_5 = 460·2.			
Dipyridinium molybdenyl pentachloride.			
1·640	0·0365	8·77	51·23
0·765	0·0170	9·00	49·92
0·417	0·0093	9·84	45·66
M for $(C_5H_6N)_2MoOCl_5$ = 449·3.			
Diquinolinium molybdenyl pentachloride.			
1·150	0·0203	9·01	62·96
0·558	0·0098	9·89	57·35
0·269	0·0047	10·45	54·30
M for $(C_9H_8N)_2MoOCl_5,H_2O$ = 567·3.			

TABLE II.

	$(NH_4)_2MoOCl_5$.				Rb_2MoOCl_5.			
v	199·2	796·8	1593·6	3187·2	51·14	409·1	818·2	1636·4
μ	755·3	865·6	916·8	948	689	849	910	973
	K_2MoOCl_5.				$[(CH_3)_2NH]_2MoOCl_5$.			
v	36·54	292·3	584·6	1169·3	59·76	239·0	478·1	1912·3
μ	676·6	834·3	897·3	954	644	757	836	935
	$(C_5H_6N)_2MoOCl_5$.				$(C_9H_8N)_2MoOCl_5$.			
v	54·7	437·5	875	1751	152	1216	2432	
μ	659·1	842·6	914·7	959	693	870	929	

that the complex ion $MoOCl_5''$ is unstable, and that ionisation and hydrolysis occur in accordance with the following scheme :

$$R_2[MoOCl_5] + H_2O \rightleftharpoons R[MoOCl_4,H_2O] + RCl,$$
$$R[MoOCl_4,H_2O] + H_2O \rightleftharpoons [MoOCl_3,2H_2O] + RCl,$$
$$[MoOCl_3,2H_2O] + H_2O \rightleftharpoons [MoO(OH)Cl_2,2H_2O] + HCl,$$
$$[MoO(OH)Cl_2,2H_2O] + H_2O \rightleftharpoons [MoO(OH)_2Cl,2H_2O] + HCl,$$
$$\rightleftharpoons [MoO_2Cl,3H_2O] + HCl,$$
$$[MoO_2Cl,3H_2O] + H_2O \rightleftharpoons [MoO_2(OH),3H_2O] + HCl,$$

Whence, at infinite dilution :

$$R_2[MoOCl_5] + 5H_2O \rightleftharpoons [MoO_2(OH),3H_2O] + 2RCl + 3HCl.$$

In the first place, it is seen from such a scheme of ionisation that 10 ions should result at infinite dilution and that the osmotic factor should be 11. These theoretical deductions are in accordance with the experimental data. The ionic velocities at 0° deduced from the values at 18° (Landolt–Börnstein, " Tabellen," 1923, ii, 1104) are : $H^{\cdot} = 227{\cdot}6$; $Cl' = 40{\cdot}0$; $Rb^{\cdot} = 41{\cdot}5$; $NH_4^{\cdot} = 38{\cdot}4$. From the ammonium and rubidium salts, for example, which on the proposed scheme of ionisation should each yield at infinite dilution 2 metal (or ammonium), 3 hydrogen, and 5 chlorine ions, a molecular conductivity of 959·6 and 965·8, respectively, would be expected. Since, for the pyridinium ion an ionic velocity of 20 is obtained at 0° (Landin, *J. Chim. physique*, 1907, **5**, 592), the value of μ_∞ for the pyridinium complex salt should be 923. Reference to the experimental values shows that they are in good agreement with these theoretical values. Additional confirmation of this scheme of ionisation for the complex salts is afforded by the isolation of the intermediate products $R[MoOCl_4,H_2O]$, $R[MoO_2Cl_2,2H_2O]$, and an oxychloride, $[Mo_2O_4(OH)Cl,4H_2O]$, which may be considered as derived from the intermediate substances $[MoO_2Cl,3H_2O]$ and $[MoO_2(OH),3H_2O]$.

Salts of the Type $R[MoOCl_4,H_2O]$.

Hitherto only bromides of this type of co-ordination compound have been isolated. The first chloride of this type, *monotrimethylammonium molybdenyl tetrachloride*, was obtained as follows :

75 C.c. of the molybdenum trioxide solution, electrolytically reduced to the quinquevalent stage, were concentrated on a water-bath under diminished pressure to 20—25 c.c. 30 C.c. of a solution of trimethylamine hydrochloride (11 g.) were now admitted by releasing the vacuum, and the mixture was heated to boiling under diminished pressure. The solution was then saturated with hydrogen chloride while it was being cooled, finally in a freezing-mixture, and the emerald-green crystals thus obtained were filtered, washed with

concentrated hydrochloric acid, and dried in a vacuum over solid potassium hydroxide and phosphoric oxide {Found: Mo, 28·8; Cl, 42·6; N, 4·24; C, 10·8; H, 3·67. $(CH_3)_3NH[MoOCl_4,H_2O]$ requires Mo, 28·9; Cl, 42·7; N, 4·22; C, 10·9; H, 3·62%}.

Molecular-weight Determinations.—The molecular weight was determined by the depression of the freezing point of air-free water.

G. of substance per 100 g. of water.	Conc. (mol. per 1000 g. water).	Osmotic factor.	Apparent mol. wt.
1·940	0·0585	6·97	47·60
0·787	0·0237	7·05	47·07
0·199	0·0060	8·07	41·13

M of $(CH_3)_3NH[MoOCl_4,H_2O]$ = 331·8.

Molecular Conductivities.

v	35·6	71·2	142·4	284·8	569·6	1139·2	2278·4	4556·8
μ	580	614	657	706	773	832	849	874

The calculated value for μ_∞ at 0° is *ca.* 880 on the scheme of ionisation and hydrolysis previously outlined, for there are produced 1 trimethylammonium, 4 chlorine, and 3 hydrogen ions, whilst the osmotic factor should be 9. The experimental results are clearly in accordance with the theoretical predictions.

Salts of the Type $[MoO_2X_2,2H_2O]R$.

In the scheme of ionisation proposed for the complex salts of quinquevalent molybdenum, the co-ordination compound $[MoO_2Cl_2,2H_2O]H$ was postulated as an intermediate product. Although this acid has not been isolated, its derivatives have been obtained in reactions involving the green complex salts.

Barium Oxalomolybdite.—Bailhache (*Bull Soc. chim.*, 1903, **68**, 161) prepared this compound by reducing ammonium molybdate in hydrochloric acid with red phosphorus, and formulated it as $BaH_2(MoO)_2(OH)_6(C_2O_4)_2,H_2O$. Viewed in the light of Werner's co-ordination theory, however, a more rational formulation and name for the substance are obtained if the molybdenum is assigned a co-ordination number of six. The new formula $Ba[MoO_2(C_2O_4),2H_2O]_2,H_2O$ clearly shows the relationship to the co-ordination compound $H[MoO_2Cl_2,2H_2O]$, and requires the name barium molybdenum dioxyoxalate. The probable correctness of this formulation and the importance of this salt can be appreciated from Bailhache's statement (*loc. cit.*) that it is produced when diammonium molybdenyl pentachloride is treated with oxalic acid and barium chloride. No details of the method were given, but experiments showed that the salt could be satisfactorily isolated by the following method:

30 C.c. of an aqueous solution of oxalic acid (1·2 g.) were added to 30 c.c. of a solution of diammonium molybdenyl pentachloride (3·5 g.), and the mixture was warmed. To the dark red solution produced, barium chloride (1·1 g.) in 60 c.c. of water was added, and on boiling, with constant stirring, a red, crystalline solid separated in good yield, which was washed with warm water and dried; it proved to be the required compound {Found: Ba, 20·8; Mo, 29·0; C, 7·28; H, 1·50. Calc. for $Ba[MoO_2(C_2O_4),2H_2O]_2,H_2O$: Ba, 20·8; Mo, 29·1; C, 7·25; H, 1·52%}.

Pyridinium Molybdenum Dioxydichloride.—Sand and Burger (*loc. cit.*) noticed that when their green pyridinium molybdenyl pentachloride was boiled with alcohol, copper-red crystals separated on cooling. This compound contained Mo, 31·7; Cl, 23·68; N, 4·75; C, 22·05; H, 2·90%, and it was assigned the formula $Mo(OH)_3Cl_2,C_5H_5N$, which requires Mo, 32·32; Cl, 23·09; N, 4·71; C, 20·20; H, 2·69%. Although the analytical figures do not show very close agreement with those demanded by theory, yet the empirical formula assigned to the substance by Sand and Burger has now been shown to be correct. It should be written, however, as $C_5H_6N[MoO_2Cl_2,H_2O]$, whereby it is characterised as the pyridinium salt of the acid $H[MoO_2Cl_2,2H_2O]$. A pure product was obtained by the following method: Freshly prepared dipyridinium molybdenyl pentachloride was added to boiling alcohol (95%) until the solution turned dark red and further solid dissolved with difficulty. On filtering and allowing the clear liquid to cool, a light red substance separated which gave Mo : Cl = 1 : 2·1 and proved to be an impure product. This was removed, and the mother-liquor, on concentration to small bulk and cooling, gave copper-red needles, which were washed with alcohol (95%) and dried in a vacuum over phosphoric oxide. The water content of the crystals varied with different samples, whilst the colour deepened with increasing water content (Found: Mo, 33·88; Cl, 24·97; N, 4·93; C, 21·5; H, 2·34. Calc. for $C_5H_6N[MoO_2Cl_2],0·25H_2O$: Mo, 33·88; Cl, 25·02; N, 4·94; C, 21·2; H, 2·29%). That this pyridinium salt and barium molybdenum dioxyoxalate are similarly constituted is readily demonstrated as follows: 3 G. of pyridinium molybdenum dioxydichloride in 50 c.c. of water were warmed with an aqueous solution of oxalic acid (1·2 g. in 30 c.c.). 1·1 G. of barium chloride in 60 c.c. of water were now added and the mixture was heated to boiling. The corresponding barium compound separated in good yield (Found: Ba, 21·4; Mo, 29·7. Calc. for $Ba[MoO_2(C_2O_4),2H_2O]_2$: Ba, 21·4; Mo, 29·9%). It will be noticed that the water content is less than that in the sample prepared from the green complex salt.

Molecular-weight Determinations.

G. of substance per 100 g. of water.	Conc. (mol. per 1000 g. water).	Osmotic factor.	Apparent mol. wt.
2·489	0·0838	3·45	86·06
1·148	0·0387	3·73	79·60
0·692	0·0233	3·90	76·12
0·222	0·0075	4·82	61·60

M for $C_5H_6N[MoO_2Cl_2,H_2O] = 296·9$.

Molecular Conductivity.—This was determined at 0° :

v	20·56	41·12	164·5	329	1316
μ	185	210·6	275·1	312·0	336·0

These two results find an adequate explanation on the assumption that in aqueous solution the pyridinium salt undergoes ionisation and hydrolysis in accordance with the scheme :

$$[MoO_2Cl_2,2H_2O]C_5H_6N + H_2O \rightleftharpoons C_5H_6NCl + [MoO_2Cl,3H_2O]$$
$$\rightleftharpoons C_5H_6N^{\cdot} + Cl' + [MoO_2Cl,3H_2O],$$
$$[MoO_2Cl,3H_2O] + H_2O \rightleftharpoons [MoO_2(OH),3H_2O] + H^{\cdot} + Cl'.$$

Hereby, in dilute solutions, an osmotic factor of 5 should be obtained, whilst conductivity measurements, due to a pyridinium ion, 2 chlorine ions, and 1 hydrogen ion, should give μ_∞ = approx. 327·6. The experimental results are in close agreement with the theoretical values and support the scheme of hydrolysis outlined above.

Dimolybdenum Tetraoxyhydroxychloride.—The isolation of this salt, $Mo_2O_4(OH)Cl$, formed an important link in the chain of evidence for the scheme of ionisation and hydrolysis proposed for the green complex salts.

Preparation. The reddish-brown solution of quinquevalent molybdenum, obtained by the electrolytic reduction of 150 c.c. of molybdic acid solution, was concentrated on a water-bath under diminished pressure until a dark, viscous mass was obtained. Pure, dry acetone was admitted in small portions with frequent shaking and warming, until the mass just dissolved, giving a deep brown solution. This was poured with constant stirring into a large volume of dry ether and a bulky reddish-brown precipitate separated, which was washed with dry ether and kept over solid potassium hydroxide in a vacuum [Found : Mo, 51·6; Cl, 9·54; Mo : Cl = 2 : 1. $Mo_2O_4(OH)Cl,3·5H_2O$ requires Mo, 51·7; Cl, 9·55%].

Valency. A solution of the compound in dilute sulphuric acid was titrated with standard permanganate according to Reinhardt's method, and required t_1 c.c. A solution of the same concentration was passed through the reductor (J., 1923, **123**, 969) and required

t_2 c.c. of permanganate. The valency is given by $(6 - 3t_1/t_2)$. Found: $t_1 = 7{\cdot}58$ c.c.; $t_2 = 22{\cdot}79$ c.c. Hence the molybdenum is quinquevalent.

Properties. The new chloride is a reddish-brown powder, readily soluble in water and in alcohol, giving deep reddish-brown solutions which on dilution become bright yellow. The aqueous solution is acid to litmus and reduces solutions of silver salts. The brown aqueous or alcoholic solutions of the compound turn emerald-green on saturation with hydrogen chloride, and complex salts of the type R_2MoOCl_5 may be isolated from them. On heating, the chloride decomposes with evolution of hydrogen chloride.

Molecular-weight Determinations.—These were determined in air-free water.

G. of substance per 100 g. of water.	Conc. (mol. per 1000 g. water).	Osmotic factor.	Apparent mol. wt.
1·193	0·0314	1·85	205·7
0·656	0·0172	2·03	187·5
0·483	0·0127	2·41	157·9

M for $Mo_2O_4(OH)Cl,4H_2O = 380{\cdot}5$.

These results indicate that two ions are present in the more concentrated solutions and three individuals in the more dilute. This is satisfactorily explained by the progressive hydrolysis

$$[Mo_2O_4(OH)Cl] + H_2O \rightleftharpoons [Mo_2O_4(OH),H_2O]Cl \rightleftharpoons [Mo_2O_4(OH),H_2O]^{\cdot} + Cl',$$

or $$[Mo_2O_4(OH)Cl] + H_2O \rightleftharpoons [Mo_2O_4(OH)_2] + H^{\cdot} + Cl'.$$

Conclusions.

The results obtained from the determinations of molecular weights and molecular conductivities of a wide range of co-ordination compounds of the formula $R_2[MoOCl_5]$ leave little doubt that the scheme of hydrolysis and ionisation outlined in this paper substantially explains their behaviour in aqueous solution. It receives added support from the physico-chemical measurements made with compounds typical of the intermediate stages of the hydrolysis. Still more convincing proof of the correctness of the scheme is that it allows the formulation and characterisation of salts previously known, and derived from the green complex salts, but which had hitherto lacked systematisation. In a paper by Scagliarini (*Atti R. Accad. Lincei*, 1925, **1**, 676), the isolation of two salts, formulated as $MoOCl_3,C_5H_5N$ and $2\left[(NH_4)_2\left\{Mo\begin{matrix}(OH)_4\\Cl_3\end{matrix}\right\}\right] + C_6H_{12}N_4,HCl$, by

reactions involving the complex salt $(NH_4)_2[MoOCl_5]$ has been made the basis of the following scheme of hydrolytic decomposition:

$$R_2MoOCl_5 + H_2O = R_2Mo(OH)_2Cl_5 \xrightarrow{H_2O} R_2Mo(OH)_3Cl_4 + HCl \xrightarrow{H_2O}$$
$$R_2Mo(OH)_4Cl_3 + HCl \xrightarrow{H_2O} R_2Mo(OH)_5Cl_2 + HCl \xrightarrow{H_2O}$$
$$R_2Mo(OH)_6Cl + HCl.$$

Such a scheme does not adequately explain the physico-chemical results obtained in the present paper, nor does it elucidate the constitution of intermediate products, which are assigned co-ordination numbers of 7. The analyses quoted by Scagliarini (*loc. cit.*) for the compounds he isolated involve only determinations of molybdenum, chlorine, and nitrogen, and do not show very satisfactory agreement with the calculated values. Confirmation of the isolation of the salt $MoOCl_3,C_5H_5N$ would be of interest, for as yet $MoOCl_3$ has not been obtained.

The authors wish to express their thanks to the Chemical Society and the University of Birmingham Research Committee for grants in aid of this investigation.

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CCLXXXVI.—*The Routine Preparation of Low-conductivity Water.*

By GUY D. BENGOUGH, JOHN M. STUART, and ALFRED R. LEE.

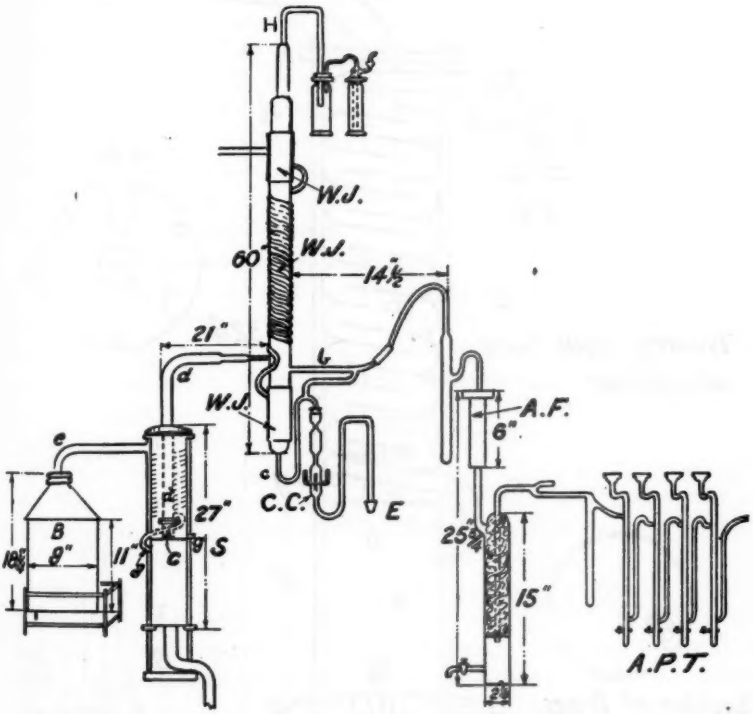
THE present communication gives details of improvements in the construction of Bourdillon's still for conductivity water (J., 1913, **103**, 791), by which it has been found possible to produce a large daily supply of such water of high quality.

Bourdillon's still delivered 7—8 litres of 0·2 gemmho conductivity in a single distillation from Oxford tap-water, and, although even the best water obtained showed conductivities as high as 0·11 gemmho from tap-water and 0·09 from distilled water at 18°, the authors constructed a precisely similar still with a view to effect improvements.

The water from this still sometimes had conductivities similar to those obtained by Bourdillon, but a regular daily supply did not maintain this degree of purity for any considerable period, even with frequent attention to small adjustments. The causes of the rises in conductivity appeared to be (*a*) minute air-leaks in some parts of the apparatus, *e.g.*, round the rubber stoppers, (*b*) inadequate trap-

ping of spray, or (*c*) "creeping" of water from the trap to the condenser. Air-leaks generally occurred between the spray-trap and the rest of the apparatus even when the rubber stoppers used by Bourdillon were replaced by pipe-unions, and "creeping" of water took place to a surprising extent, especially when there were considerable fluctuations of pressure in the still.

FIG. 1.



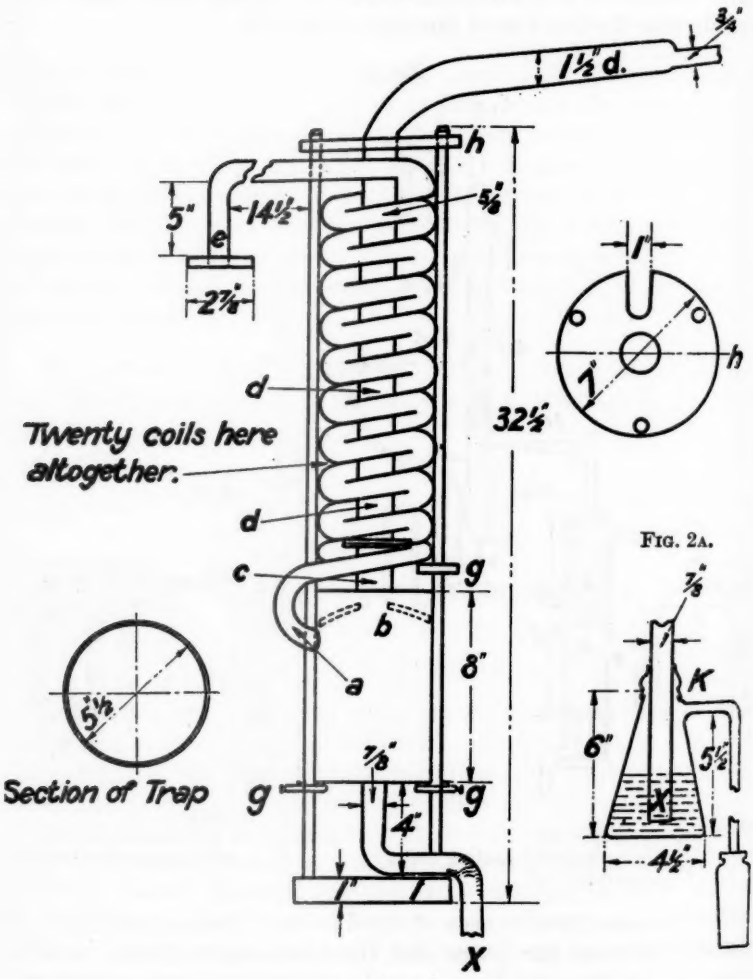
B. Boiler.
S. Spray trap.
W.J. Water jacket and cooling coils.
C.C. Conductivity cell.
A.F. Air filter.
A.P.T. Air purification train.
E. Outlet for purified water.

To eliminate these causes of trouble, the whole of that part of the still between the boiler and the block-tin condenser was redesigned; at the same time, some improvements were made in the air-purification train. The still in its final form is shown in Fig. 1.

The boiler, *B*, is made of 18-gauge (1·2 mm. thick) copper sheet, tinned on the inside. It is connected to the rest of the apparatus by two circular flanges, 7·0 cm. in diameter, soldered both to it and to the copper pipe, *e*. A ring of "hallite" packing is used between the flanges, which are held together by six bolts. (A

flange is shown in Fig. 2, *e*.) The boiler holds 10 litres of water, which is introduced, together with the ground potassium bisulphate, by separating the flanges. This is the only joint on the still that

FIG. 2.



Dimensioned sketch (not drawn to scale).

FIG. 2A.

need be broken during several months' running. The available waters were a hard London tap-water, and a supply which contained traces of oil. The former was objectionable owing to the possible formation of heavy boiler-scale, so the latter was used

after a preliminary rough distillation with potassium permanganate and caustic potash in a simple form of still.

From the boiler, the steam passes through the copper tube, *e* (Figs. 1 and 2), to the trap, which has been redesigned and very solidly constructed, as shown on an enlarged scale in Fig. 2. The tube, *e*, is of 1·3 cm. internal diameter and is bent into 20 coils each of 12·5 cm. diameter, and its end is brazed into the copper trap tangentially so as to give circular motion to the steam entering the trap at *a*. A circular conical baffle-plate, *b*, is inserted above this. The steam outlet at *c* is provided with a 7 cm. circular flange (not shown in Fig. 2) which is bolted to " hallite " jointing and a similar flange on the block-tin tube, *d*. This tube has an internal diameter of 4 cm. and is soldered to the condenser. The ample width of this tube prevents any trapping of water; in the earlier still, a long, narrow, coiled tube was used and arranged outside the copper coil, but water occasionally accumulated in the bends and caused violent fluctuations of pressure in the still.

The copper coil and trap are lagged with cotton waste and asbestos sheet and are held in place by three adjustable supports, *g*, which can be clamped to three vertical brass rods. These brass rods are rigidly fixed into a heavy cast iron base, *I* (Fig. 2).

A brass plate, *h*, is bolted to the tops of the rods, and, together with a flange, provides support for the central tin tube. At first, the water from the submerged outlet tube, *X* (Fig. 2), was merely allowed to run into an open beaker, but the best water was not obtained until a definite air-trap and non-return valve were used, as shown in Fig. 2A.

The main block-tin condensing column is similar to that of Bourdillon, but the arrangements at the lower end have been altered as shown in Fig. 1; *d* is the steam inlet leading from the trap and is soldered into the main column, *b* is the inlet for purified air, and *c* the outlet for the conductivity water; *W.J.* consists of two glass water-jackets connected together by a long coil of compo-tubing carrying a stream of water. The conductivity-measuring vessel *C.C.* is fixed on to *c* by a rubber stopper. The advantage of this arrangement is that the water does not become saturated with air in the cold as in Bourdillon's method, and consequently air-bubbles do not form on the electrodes of the conductivity cells.

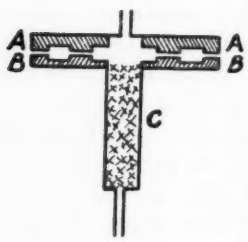
On the upper part of the tin condenser is a narrow tin tube, *H*, soldered to the main column and joined by a rubber connexion to a glass tube leading into a bottle. A second bottle is connected so that the escaping air bubbles out through a shallow layer of distilled water. If a sudden diminution of pressure occurred in the

still, the water in the second bottle would merely be sucked back into the first and not into the still.

The rate at which bubbles pass through the water serves as a rough indication that the purified air is passing satisfactorily through the still. Before distillation is stopped, the second bottle should be replaced by a soda–lime tube.

The Weiland purification trains, *A.P.T.* in Fig. 1, contain *N*-sulphuric acid, caustic potash solution, and distilled water; two are used in parallel, as it was found advisable to use a much faster stream of air than that used by Bourdillon. Recently Weiland's design has been modified: the columns containing the glass beads are now 2·5 cm. in diameter and are pinched in near the tops to retain the beads; the funnels and taps have been increased in size. The air passes through a dust-filter (*A.F.*, Fig. 1) constructed as shown in Fig. 3. This filter is a modification of one described in the Meteorological Office Report of the Advisory Committee on Atmospheric Pollution, 1916—17. It is constructed of brass, and the air first passes through the tube *C*, which is filled with special jewellers' wool, and then through a disc of special blotting paper (Ford 428 Mill) inserted between brass discs *A* and *B*, which have circular and radial grooves cut in them as shown. *A* and *B* are bolted together and the joint is waxed over externally.

FIG. 3.



The course of an actual distillation was as follows: Ten litres of laboratory distilled water were placed in the boiler with 20 g. of powdered potassium bisulphate, and heated to boiling; the "hallite" joint softened in the steam, and the boiler was then connected with the still.

The heating was adjusted so that the conductivity cell was filled and emptied every 9 or 10 minutes. This rate of delivery corresponds to the production of about 0·75 litre of water per hour and should not be greatly exceeded; if the still is run too rapidly, a trace of spray seems to get into the condenser during distillation.

The conductivity of the water was determined by the standard bridge method, a galvanometer being used to detect the zero position. This was possible because the conductivity was so low that only very small currents passed, and polarisation effects were negligible. The cells in which measurements were made were standardised with *N*/50-solutions of potassium chloride. The possible errors in the values for conductivities given in Table I are within $\pm$ 5%. The table gives the values (in gemmhos) of the specific conductivity, κ,

of each batch of water reaching the conductivity cell in a typical run of the still, the purified air being supplied at a rate of about 22·5 litres per hour, and the temperature of the water being about 15°.

TABLE I.

Batch No.	κ.	Batch No.	κ.	Batch No.	κ.	Batch No.	κ.
1	0·17	10	0·057	19	0·055	28	0·054
2	0·13	11	0·055	20	0·055	29	0·055
3	0·078	12	0·062	21	0·055	30	0·059
4	0·077	13	0·057	22	0·055	31	0·063
5	0·062	14	0·052	23	0·054	32	0·067
6	0·059	15	0·050	24	0·054	33	0·071
7	0·055	16	0·052	25	0·054	34	0·084
8	0·072	17	0·054	26	0·065		
9	0·059	18	0·055	27	0·054		

Batches 3—33 inclusive, amounted to 4040 c.c. The volume of waste water collected at the "run off" from the steam trap was 2485 c.c.

In other runs, conductivities as low as 0·045 gemmho at 18° have been obtained. This figure is not much inferior to the best values of Kohlrausch and Heydweiller (0·040 at 18°) (*Pogg. Ann.*, 1894, **53**, 223) who distilled in a vacuum in an apparatus which was only adapted to give a small quantity of the purified water. The authors' still has been in constant use for more than 2 years and requires very little attention other than the periodic renewal of the solutions in the air-purification train. It will regularly produce about four litres a day of water with a conductivity of about 0·065 gemmho.

The authors wish to express their grateful thanks to Mr. H. R. Raikes, who placed his great experience at their disposal when constructing both the still and the apparatus for measuring conductivities.

The work was carried out in the Metallurgical Laboratory of the Royal School of Mines, as part of a research directed by the Corrosion of Metals Research Committee of the Department of Scientific and Industrial Research, and the authors wish to thank the Chairman, Professor H. C. H. Carpenter, for the many facilities afforded.

[*Received, June 18th*, 1927.]

CCLXXXVII.—*The Action of Bromine on Dimethylpyrone.*

By John Norman Collie and Louis Klein.

The constitution of the pyrone nucleus is of importance in that many interesting compounds are derived from it. Bromine reacts with it at once, but does not give ordinary addition products, and similarly there is no indication that any ethylenic linkages are present in dimethylpyrone.

10 G. of dimethylpyrone (1 mol.) and 13 g. of bromine (1 mol.) were allowed to react in chloroform solution, and the mixture became orange-coloured and slightly warm. The solvent was evaporated at the ordinary temperature, and the resulting bright orange-coloured, crystalline solid was washed with water, which removed dimethylpyrone hydrobromide, together with a small quantity of some pyrone compound containing bromine—this was probably the bromodimethylpyrone, but owing to its high solubility it could not be separated from the hydrobromide.

The orange compound (yield, 10 g.) was best recrystallised from acetic acid or chloroform; m. p. 136° (Found: C, 34·1; H, 3·8; Br, 49·5; *M*, cryoscopic in naphthalene, 456, 479. Calc. for $C_{14}H_{17}O_4Br_3$: C, 34·4; H, 3·5; Br, 49·1%; *M*, 489).

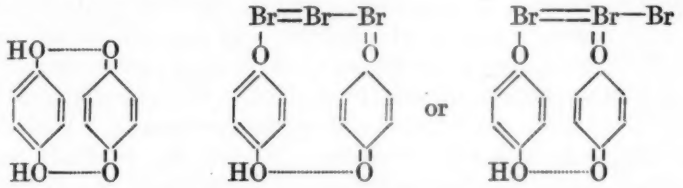
This compound has also been obtained by Hantzsch and Denstorff (*Annalen*, 1906, **349**, 39), who only gave a bromine determination, by the action of bromine on dimethylpyrone hydrobromide. They recognised it as a perbromide, and we have confirmed this by obtaining several characteristic reactions for perbromides, some of which were carried out quantitatively, although in the reaction with ammonia only about two-thirds of the theoretical amount of nitrogen were evolved.

On being warmed with water, the compound loses its colour and dissolves, except for a small quantity of a yellow oil (Found: ionisable Br, 37·0%). On standing with water for 3 days, however, only a trace of the yellow oil remained, and the ionisable bromine was then 46·9%. The yellow *oil* does not crystallise on keeping and cannot be distilled (Found: Br, 58·1. $C_7H_6O_2Br_2$ requires Br, 56·7%). Aqueous potassium hydroxide behaves in a similar manner to water (Found: ionisable Br, 46·1%).

The action of heat on the orange compound is complex. If kept just at its m. p. it loses colour, and then solidifies on cooling. If more strongly heated, it chars and gives off hydrogen bromide, the product being almost entirely soluble in water, and consisting chiefly of dimethylpyrone hydrobromide, mixed with a small

quantity of (probably) the bromodimethylpyrone, which, however, could not be separated. The small amount of insoluble *substance* was a yellow, non-crystallisable oil (Found : Br, 61·4%).

The orange compound resembles quinhydrone in some respects, *e.g.*, reaction with water and possession of colour, and this suggests a similarity in molecular constitution :



The action of a larger amount of bromine on dimethylpyrone was tried : 10 g. of the pyrone and 26 g. of bromine in chloroform solution. After evaporation of the chloroform, the residue was treated with water, and the insoluble portion recrystallised from dilute alcohol. A colourless compound resulted; m. p. 163° (Found : C, 29·8; H, 2·6; Br, 56·3. Calc. for $C_7H_6O_2Br_2$: C, 29·8; H, 2·1; Br, 56·7%). This compound had been previously obtained by Feist and Baum (*Ber.*, 1905, **38**, 3562). On being boiled with water it gives bromoacetone. It does not form salts with acids, and its solution in alcohol does not give an immediate precipitate with silver nitrate. On being heated with sodium ethoxide solution, it turns deep red in colour.

If excess of bromine is allowed to react with dimethylpyrone in the absence of a solvent, the mixture becomes warm, and on boiling it evolves hydrogen bromide and eventually becomes solid. Extraction with alcohol leaves a crystalline residue, which is almost insoluble in most solvents. From hot acetic anhydride, however, a *substance* separates in bunches of needles, m. p. 229° (darkening at 227°) (Found : C, 19·3; H, 1·2; Br, 71·5. $C_7H_4O_2Br_4$ requires C, 19·1; H, 0·9; Br, 72·7%). This compound is very stable, being unaffected by metallic sodium in boiling benzene solution, or by warm concentrated sulphuric or nitric acids, from solutions in which it is precipitated unchanged on the addition of water. Heating with ammonia in a sealed tube at 140° or boiling with sodium hydroxide solution, however, effect decomposition, which is very far-reaching in the former case.

A curious iodine compound was obtained by one of the authors (J., 1900, **77**, 1116; 1921, **119**, 1550) by the action of iodine on the barium salt of diacetylacetone. Bromine has now been found to give a similar compound; it was added slowly with shaking to an aqueous suspension of the barium salt (45 g.), and dilute hydro-

chloric acid then precipitated 9 g. of the *substance*, which was recrystallised from dilute alcohol; m. p. 106°; b. p. *ca.* 310° (decomp.) (Found: C, 38·6; H, 3·4; Br, 36·6. *M*, microcryoscopic in camphor, 236. $C_7H_7O_3Br$ requires C, 38·4; H, 3·2; Br, 36·5%; *M*, 219). In all its reactions it resembles the iodine compound. It can be boiled with the strongest sodium hydroxide, or with sodium ethoxide, without decomposition, and is reprecipitated on adding an acid. Cold concentrated sulphuric acid does not decompose it, and although it does not react with cold sodium carbonate solution, on warming, carbon dioxide is evolved. With bleaching-powder solution, it gives a precipitate of calcium carbonate. With ferric chloride, it gives a red precipitate. It can also be made by the action of bromine on the sodium salt of diacetylacetone. It forms a *monobenzoyl* derivative, m. p. 112° (Found: C, 51·8; H, 3·7; Br, 24·5. $C_{14}H_{11}O_4Br$ requires C, 52·0; H, 3·4; Br, 24·8%); and with phenylhydrazine it yields a *compound*, m. p. 142° (decomp.) (Found: N, 8·8; Br, 26·3. $C_{13}H_{13}O_2N_2Br$ requires N, 9·1; Br, 25·9%).

An unsuccessful attempt was made to produce a corresponding chlorine compound by the action of chlorine on the barium salt of dimethyl pyrone.

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UNIVERSITY COLLEGE, LONDON. [*Received, June 30th*, 1927.]

CCLXXXVIII.—*The Application of the Hydrogen Electrode to Organic Bases: Piperidine, and its Use as an Alkaline Buffer.*

By EDMUND B. R. PRIDEAUX and FRANK L. GILBERT.

THE dissociation constants of organic bases rest on conductivity determinations alone, whilst the hydrogen-ion concentrations of their partly neutralised solutions are either calculated from these constants or determined by colorimetric methods. It would seem desirable to test these results with the hydrogen electrode, as has been done in the case of acids. It has long been known that this electrode is untrustworthy with ammonia and some amines (Bottger, *Z. physikal. Chem.*, 1899, **24**, 253), and it has also been stated (Kolthoff, *Biochem. Z.*, 1925, **162**, 289) that the alkaloids are susceptible to catalytic reduction at the surface of a hydrogen electrode. The possibility of carrying out an electrometric titration on hydrazine has, however, been established by Gilbert (*J. Amer. Chem. Soc.*, 1924, **46**, 2648). This base is unstable in most respects, but is resistant to reducing agents. Although the numerical results

were not given in the paper, one can infer that the first constant was in fairly good agreement with the value, 3×10^{-6}, based on Bredig's measurements of conductivity.

Piperidine seemed to be eminently suitable for testing the constant derived from conductivity, since it is a moderately strong base which obeys the dilution law, and it was deemed to be stable towards platinum–hydrogen. The dissociation constant according to Bredig is $1{\cdot}6 \times 10^{-3}$, and $\lambda_0 = 216$, expressed in modern units (*Z. physikal. Chem.*, 1894, **13**, 191). The value used by Hantzsch and Sebaldt (*ibid.*, 1900, **33**, 129) is 232 at 25°. In the case of the hydrochloride, at $v = 1024$, $\lambda = 110$; if 2·5 units be added, according to the usual rule, $\lambda_0 = 112{\cdot}5$; since the mobility of the chlorine ion is 75·5, that of the piperidinium ion is 37·0, and, that of the hydroxyl ion being 196, λ_0 for piperidine is found to be 233. On combining this with the λ values of Bredig (converted into ohms) for $v = 32$ and 256, one finds $K = 1{\cdot}42 \times 10^{-3}$ and $1{\cdot}30 \times 10^{-3}$, respectively. These are rather higher than the constants of Hantzsch and Sebaldt (*loc. cit.*), *viz.*:

Temp.	=	15°	20°	25°
10^3K	=	1·11	1·15	1·20

from which, by interpolation, the constant at 18° is $1{\cdot}14 \times 10^{-3}$, $p_K = 2{\cdot}94$. We consider this constant to be a more satisfactory basis for calculations than the uncorrected constant of Bredig. We have tested its validity for expressing the p_H values obtained during neutralisation by (*a*) a potentiometric and (*b*) a colorimetric titration.

(a) *Electrometric Titration.*—The usual circuit for potentiometric titrations was set up, containing a cadmium cell, which was checked against an N.P.L. Standard, a capillary electrometer, and a metre slide wire, which had been calibrated against an accurate resistance box. A platinised platinum–hydrogen electrode of the Hildebrand type dipped into an open beaker which contained the solution of piperidine. The other half-cell was an $N/10$-potassium chloride–calomel electrode, the two solutions being connected by a salt bridge of saturated potassium chloride–agar.

To the $N/10$-piperidine solution, N-hydrochloric acid was added with stirring. The balance point on the bridge-wire became steady at once, and readings were taken after each addition of acid. The *E.M.F.*, E_c in table, of the hydrogen half-cell against an electrode in N-hydrogen ion is equal to the *E.M.F.*, E in table, corresponding to the balance-point minus 0·338. The readings are given as c.c. of hydrochloric acid added to a given volume of piperidine:

c.c.	=	2·1	2·45	2·75	3·0	3·2	3·4
E	=	0·962	0·943	0·914	0·845	0·502	0·461
E_c	=	0·624	0·605	0·576	0·507	0·164	0·123

$\Delta E/\Delta C$ assumes a high value between 3·0 and 3·2 c.c.; the subsequent readings correspond to solutions beyond the equivalence point.

The possibility of a satisfactory electrometric titration is thus demonstrated. Some of these results were used in determining p_K (see below), the following p_H values being calculated from $E_c/0{\cdot}058$:

E_c =	0·624	0·605	0·576	0·507	0·164	0·123
p_H =	10·75	10·45	9·92	8·73	2·84	2·12

Electrometric Determination of K.—Since the middle part of the neutralisation is of particular importance in determining K, another experiment was carried out (with a different volume of piperidine) from an earlier stage in the neutralisation and with 0·55N-acid, in order to obtain a greater accuracy in the values of x, the fraction of base neutralised. The values of p_K are calculated from the equation

$$p_K = \log (1 - x)/x + p_{K_W} - p_H,$$

where p_{K_W} has its usual significance and is equal to 14·13 at 18°.

The potentiometric titration of 0·1N-piperidine with 0·55N-hydrochloric acid.

HCl (c.c.).	E_c.	p_H.	$100x$.	p_K.	HCl (c.c.).	E_c.	p_H.	$100x$.	p_K.
0·65	0·682	11·8	17·8	2·99	2·10	0·637	10·95	57·4	3·05
0·95	0·672	11·6	26·0	2·98	2·40	0·620	10·75	66·0	3·09
1·24	0·665	11·43	33·9	2·99	2·65	0·607	10·55	73·3	3·14
1·60	0·652	11·23	43·7	3·00		0·605	10·45	80	3·09
1·85	0·645	11·1	51·0	3·01		0·576	9·92	90	3·26
1·95	0·640	11·05	53·4	3·02					

Thus the potentiometric constant is distinctly lower (p_K higher) than that derived from conductivity results; the constancy is very satisfactory, the trend up to $x = 0{\cdot}50$ being very slight, less indeed than in the case of most acids. Thus it has been shown by Michaelis and Kruger (*Biochem. Z.*, 1921, **119**, 307) that the p_K of acetic acid when 50% neutralised is 4·665, whilst that of the free acid is 4·733; there is therefore a decrease of 0·068 in p_K, or an increase in the constant. Although it is not possible to determine the potentiometric p_K with sufficient accuracy on aqueous solutions of free piperidine, we do know that the change of p_K over a large range of neutralisation is only about 0·02. If, however, p_K of the pure base is 2·94, the difference between this and the value prevailing at 50% neutralisation is 0·07—of the same order as the difference for acetic acid, but in the opposite direction. While, therefore, the constant increases during neutralisation in the case of typical weak acids, it decreases in the case of this weak base. It is intended to test other bases,

in order to find whether this behaviour is characteristic of the class.

The increases in the constants of acids may be plausibly attributed to the presence of the increasing amount of salt formed during the neutralisation, since the addition of sodium chloride, or other neutral salt, has a marked effect in the same direction (Michaelis and Kruger, *loc. cit.*).

The present effect, however, is not a salt effect, as was proved by the following experiments. Sodium chloride was added to the solutions under investigation so as to preserve a constant concentration of chloride, equal to that which would have been attained at the end of the neutralisation. Had the drift in the constant been a salt effect, the balance point would have been altered in the first stages of neutralisation, so as to give a constant p_K equal to the slightly higher value obtained in the nearly neutralised solution.

Addition of NaCl to 30 c.c. of piperidine at various degrees of neutralisation.

100 x.	Balance point on bridge, without NaCl.	Weight of NaCl added (g.).	Balance point in presence of NaCl.
10	51·2	0·158	51·2
30	49·7	0·117	49·8
50	48·7	0·088	48·7
80	46·4	0·035	46·5

Hence the *E.M.F.*'s and the p_H values are not affected by moderate amounts of neutral salt, the presence of which, therefore, does not account for the slight trend in K in the case of solutions which are more than 50% neutralised.

(b) *Colorimetric Titration.*—It is clear from the above results that the calculation of p_H during neutralisation from the constant which is based on conductivity will give numbers about 0·2 unit higher than those determined by the hydrogen electrode. It remains to be found whether these latter p_H values have the same effect on indicators as those derived from known buffer solutions.

We have selected the buffers of Ringer : 0·15N-Na_2HPO_4 + 0·1N-NaOH (p_H 11—12), and one of Sörensen's : 0·2N-$Na_2B_4O_7$ + 0·1N-NaOH or HCl (p_H 11—8). These solutions were matched against the piperidine at various stages of neutralisation, by using the B.D.H. "universal indicator," which can be made to show changes within 0·1 in p_H over the range involved. To 10 c.c. of the N/10-piperidine solution were added counted numbers of drops of the 0·55N-hydrochloric acid, from a dropping pipette, 22 drops of which were equal to 1 c.c. When the colour matched that of the buffer solution containing the same concentration of indicator, the % of neutralisation was recorded.

No. of drops.	p_H of buffer.	$100x$.	p_K.	No. of drops.	p_H of buffer.	$100x$.	p_K.
9	11·74	22·5	2·93	35	10·05	87·5	3·23
18	11·19	45	3·02	36	9·84	90	3·33
22	11·01	55	3·03	37	9·50	92·7	3·53
33	10·33	82·5	3·12	38	9·41	95·0	3·43
34	10·15	85·0	3·23	39	9·21	97·5	3·33

The values determined by the hydrogen electrode are therefore confirmed, and the slight trend in K_B is again found, the values of p_K rising more sharply when neutralisation is nearly complete.

In all the middle part of its neutralisation interval, piperidine will make an excellent buffer solution: the p_H values may be calculated from $p_K = 3{\cdot}00 \pm 0{\cdot}02$ between 15 and 55% neutralisation. In an $N/10$-solution of piperidine which has been 50% neutralised by $0{\cdot}5N$-hydrochloric acid, p_K is found, both by the hydrogen electrode and by indicators, to be $11{\cdot}10 \pm 0{\cdot}05$. This is an accurately defined reference point for the measurement of acidity.

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CCLXXXIX.—*Researches in the Menthone Series. Part V.* d-neoiso*Menthylamine.*

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THE constitutional formula of the menthylamines admits of the existence of four optically inactive and eight optically active forms, and of these the only stereoisomerides remaining to be prepared and characterised are the *neoiso*menthylamines (compare J., 1926, 2209, 2223). Wallach (*Annalen*, 1898, **300**, 278) obtained two bases, now called *l*-menthylamine and *d-neo*menthylamine, by heating *l*-menthone with ammonium formate. We regard both these bases as derivatives of *l*-menthone (*loc. cit.*); since, however, under the conditions of the experiment *l*-menthone is transformed partly to *d-iso*menthone (this vol., p. 1278), we considered that the reaction product should contain a corresponding proportion of formylated *iso*menthylamines. By applying the knowledge already acquired of the derivatives of active forms of the three known bases, we have been able to prepare from this product a new salicylidene (o-*hydroxybenzylidene*) derivative, m. p. 99—100°, $[\alpha]_D$ — 17·9°, which must be regarded as an active form of salicylidene*neoiso*menthylamine (J., 1926, 2225).

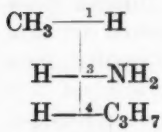
We have already shown that *d-iso*menthone, when oximated and reduced, yields *d-iso*menthylamine. *l*-Menthone yields *l*-menthyl-

amine in a similar way, and gives a mixture of *l*-menthylamine and *d-neo*menthylamine in reaction with ammonium formate. By analogy we anticipated that *d-iso*menthone would furnish *d-iso*-menthylamine and *l-neoiso*menthylamine in the last-named reaction. A careful scrutiny of the data suggests that *d-iso*menthylamine may exist in the formylated mixture, although it has not yet been isolated therefrom; the new lævorotatory salicylidene derivative, however, yielded upon hydrolysis a feebly dextrorotatory neoiso-*menthylamine*, having $[\alpha]_D + 9°$ in chloroform. The *hydrochloride* also was dextrorotatory, having $[\alpha]_D + 20{\cdot}9°$ in dilute aqueous solution. All the other derivatives, nine in number, as yet prepared from the base display rather small lævo-rotations, thus fulfilling the anticipated tendency. Since, however, the free base is dextrorotatory, we propose to name it *d-neoiso*menthylamine. The subjoined summary of melting points and specific rotatory powers indicates some of the more important relationships existing between the four optically active forms under discussion. The values of $[\alpha]_D$ were observed in water for the hydrochlorides and in chloroform for the other derivatives (compare J., 1926, 2225):

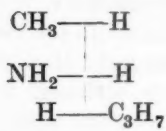
		Menthylamines.			
Derivative.		*l*-.	*d-neo*-.	*d-iso*-.	*d-neoiso*-.
Hydrochloride.	m. p.	280°	189°	250°	250°
	$[\alpha]_D$	−36·6°	+21·5°	+23·6°	+20·9°
Formyl.	m. p.	102—103	117—118	45—46	Liquid
	$[\alpha]_D$	−83·8	+53·8	+31·3	−3·9
Acetyl.	m. p.	145	169—170	77—79	99—100
	$[\alpha]_D$	−81·7	+53·0	+30·7	−2·6
Benzoyl.	m. p.	157	121·5	97—98	151
	$[\alpha]_D$	−62·8	+22·7	+18·3	−10·4
β-Naphthalene-sulphonyl.	m. p.	135	208	80—81	120
	$[\alpha]_D$	−53·3	+43·7	−2·8	−10·7
Benzylidene.	m. p.	69—70	45—46	67—68	68—69
	$[\alpha]_D$	−132·5	+61·7	+90·7	−34·2
Salicylidene.	m. p.	57—58	99—100	122	99—100
	$[\alpha]_D$	−119·2	+30·0	+77·6	−17·9

From these data it is evident that no striking general similarity exists between derivatives of the *neo*- and *neoiso*-menthylamines (compare J., 1926, 2224); further, of the four supposed benzomenthylamides described by Tutin and Kipping (J., 1904, **85**, 73) two only can now be regarded as pure substances. The data are of particular interest when considered in conjunction with the configurational scheme advanced some time ago for the menthylamines (J., 1926, 2213) and reproduced below with the amendment

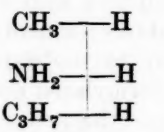
that the *trans*-configuration is adopted, in place of the *cis*-, for menthone (compare this vol., p. 1278) :



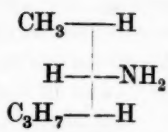
l(or *d*)-Menthylamine. (I.)



d(or *l*)-*neo*-Menthylamine. (II.)



d(or *l*)-*iso*-Menthylamine. (III.)



d(or *l*)-*neoiso*-Menthylamine. (IV.)

The adoption of configuration (II), rather than (IV), for *d*-*neo*-menthylamine (J., 1926, 2213) is now supported by the fact that the sense of the optical rotation undergoes a change throughout the series of substitution derivatives in passing from (I) to (II), but not in passing from (I) to (IV). Further generalisations may also be made which appear to accord with the suggested configurational scheme. Excluding β-naphthalenesulphon-*d*-*iso*-menthylamide, which is only feebly active, and also the hydrochlorides, which differ from the other derivatives in being ionisable, it is remarkable that the reversal of the asymmetry of carbon atom (3), carrying the characteristic amino-group, invariably changes the sign of the optical rotation. On the other hand, the reversal of the asymmetry of either of the carbon atoms (1) or (4) does not affect the sign of the optical rotation.

With regard to numerical values, it is seen that the derivatives of *trans*-menthone (I and II) possess greater rotatory powers than the derivatives of *cis*-menthone (III and IV). The most striking numerical relationships yet observed between the optical rotatory powers of corresponding members of the four series are shown by the formyl and acetyl derivatives : the sum of (I) and (IV) is in each instance practically equal in amount, but opposite in sign, to that of (II) and (III) ; similar results are obtained by comparing the sum of (I) and (III) with that of (II) and (IV), and the sum of (I) and (II) with that of (III) and (IV). These relationships do not hold for the other derivatives described in this communication, but it is hoped to pursue the subject in order to ascertain whether any definite principle of optical superposition can be discerned in this remarkable series of stereoisomerides.

The action of nitrous acid on the four types of stereoisomeric menthylamines is of particular interest. It must be recognised that the configurations which have been assigned to these substances are based largely upon the assumption that the stereoisomeride which passes most readily into a particular menthol when treated with nitrous acid is configurationally similar to that

menthol, the accompanying Δ^3-menthene being attributed in such instances to the occurrence of a Walden inversion (compare J., 1926, 2213). Thus, *l*-menthylamine and *d-iso*menthylamine yield the largest proportions of *l*-menthol and *d-iso*menthol, respectively, when treated with this reagent. Accepting these processes as the normal ones, the simultaneous formation of partly racemised *d*-Δ^3-menthene takes place through a Walden inversion, leading to the intermediate production of *d-neo*menthol and an optically active *neoiso*menthol, respectively; these alcohols, since they possess a hydrogen atom (4) in the *cis*-configurative position to the hydroxyl group (3), then undergo dehydration. The formation of partly racemised *d*-Δ^3-menthene as the main product in the remaining instances of *d-neo*menthylamine and *d-neoiso*menthylamine is accordingly regarded as the normal procedure. *l*-Menthol, which we now show to be present in small amount in the product yielded by *d-neo*menthylamine, will in this instance arise by virtue of a Walden inversion, and it appears that *d-neoiso*menthylamine yields *d-iso*menthol in a similar way.

l-Menthylamine, *d-neo*menthylamine, *d-iso*menthylamine, and *d-neoiso*menthylamine may all be utilised as sources of *d*-Δ^3-menthene, in varying yields, by the action upon them of nitrous acid (compare also Tschugaeff, *Ber.*, 1899, **32**, 3333). In these changes, carbon atom (1) alone retains its asymmetry, and a proof is thus afforded that the spatial disposition of the groups about this atom is similar in the four stereoisomeric bases concerned, as indicated in our configurational scheme. An interesting distinction between the substances is provided by the observation that the salicylidene derivatives of the menthylamines and *iso*menthylamines are phototropic, while those of the *neo*menthylamines and *d-neoiso*menthylamine are not.

Experimental.

Isolation and Characterisation of d-neoiso*Menthylamine.*—The crude oily form-*d-neo*menthylamide obtained by heating *l*-menthone with ammonium formate (Wallach, *Annalen*, 1898, **300**, 283) was dried in ether solution and distilled under diminished pressure. The first fraction consisted of menthone, but 85% of the material passed over at 160—166°/9 mm. as a clear, pale yellow syrup, which yielded about 30% of its weight of crystalline form-*d-neo*menthylamide when kept overnight in contact with dry ether. After separation of the crystals by filtration and removal of the ether, the remaining syrup had $n_D^{15°}$ 1·4840 and $[\alpha]_D^{15°}$ − 21·1° in chloroform ($c = 4·3$). Examination showed that the aqueous layer formed in the reaction could be discarded.

The clear solution obtained by hydrolysing the syrup with hydrochloric acid (*Annalen*, 1893, **276**, 308) was rendered alkaline and steam-distilled; the distillate, when carefully neutralised with hydrochloric acid and evaporated to dryness, yielded a colourless, crystalline mass of a mixture of menthylamine hydrochlorides. A non-volatile part of the alkaline mixture, having b. p. 166—176°/9 mm., $[\alpha]_D^{15°}$ + 6·6°, proved to consist of unchanged formyl derivative; selective hydrolysis had thus occurred. In subsequent hydrolyses, the boiling with concentrated hydrochloric acid was therefore continued for 4—5 hours after the syrup had dissolved; the mixture of menthylamine hydrochlorides then obtained had $[\alpha]_D^{15°}$ − 4° in water (c = 5·1).

Attempts to separate the constituents of this mixture by treatment with ether, acetone, methyl alcohol, and other organic solvents yielded unsatisfactory results. Fractional extraction of the liberated base from its solution in ether by agitation with four successive equal quantities of 0·6*N*-hydrochloric acid yielded fractions of hydrochloride having $[\alpha]_D^{15°}$ − 8·4°, − 5·3°, − 4·6°, and + 1·9°, respectively, in aqueous solution (c = 4·5). A certain degree of separation was thus effected, but the best results were obtained by preparing the salicylidene derivative directly from the mixture of hydrochlorides having $[\alpha]_D^{15°}$ − 4°, described above. When recrystallised twice from light petroleum and once from alcohol, material made in this way yielded about 8% of pure *salicylidene*-d-neois*omenthylamine*. This substance forms yellow needles, m. p. 99—100°, $[\alpha]_D^{15°}$ − 17·9° in chloroform (c = 2·3). (Found: C, 78·7. $C_{17}H_{25}ON$ requires C, 78·75%). A mixture of this derivative with about an equal amount of salicylidene-*d-neo*menthylamine (m. p. 98—99°) melted at 74—78°.

Hydrolysis was best effected by boiling the substance (12 g.) for 3·5 hours with a mixture of sulphuric acid (8·5 c.c.) and water (72 c.c.). Salicylaldehyde was extracted with ether, and d-neois*omenthylamine hydrochloride* was then prepared by steam-distilling the basified liquid into the requisite amount of dilute hydrochloric acid. The crystalline powder obtained upon evaporation was very soluble in alcohol or water, and practically insoluble in light petroleum or ether. When dissolved in boiling acetone containing a trace of methyl alcohol, it crystallised with difficulty in fine, silky needles, which did not melt below 250°; $[\alpha]_D^{15°}$ in water (c = 3·1) was + 20·9° (Found, by titration: Cl, 18·4. $C_{10}H_{21}N,HCl$ requires Cl, 18·5%). Free d-neois*omenthylamine* is a liquid which resembles the stereoisomeric menthylamines in its odour. The approximate rotatory power was determined by extracting with chloroform the base liberated from a known weight of hydrochloride

(1·669 g.); the dried chloroform solution (50 c.c.) gave $[\alpha]_D^{15°} + 9°$ ($\alpha_D^{15} + 0·30°$ in a 1-dcm. tube).

The *formyl* derivative is a viscid oil, having $[\alpha]_D^{15°} - 3·9°$ in chloroform ($c = 4·4$). The *acetyl* derivative is very soluble in organic solvents; it crystallised from light petroleum in needles which softened at 87°, melted at 99—100°, and showed $[\alpha]_D^{15°} - 2·6°$ in chloroform ($c = 2·7$). The *benzoyl* derivative crystallises from alcohol in fine, silky needles, m. p. 151°, $[\alpha]_D^{15°} - 10·4°$ in chloroform ($c = 2·3$). The β-*naphthalenesulphonyl* derivative, after three recrystallisations from alcohol, formed hard aggregates, m. p. 120°, $[\alpha]_D^{15°} - 10·7°$ in chloroform ($c = 2·9$). *Benzylidene*-d-neoiso*menthylamine* separates from hot methyl alcohol in coarse, colourless needles, m. p. 68—69°, $[\alpha]_D^{15°} - 34·2°$ in chloroform ($c = 2·0$). A mixture with benzylidene-*l*-menthylamine (m. p. 69—70°) melted at 45—51°. d-neoiso*Menthylcarbamide* crystallised from ether–light petroleum in fine needles, m. p. 115—116°, $[\alpha]_D^{15°} - 3·1°$ in chloroform ($c = 1·9$). d-neoiso*Menthylphenylcarbamide* forms small needles, m. p. 149—150°, $[\alpha]_D^{15°} - 12·1°$ in chloroform ($c = 2·5$); the pure derivative was readily obtained in 75% yield. d-neoiso*Menthylphenylthiocarbamide* crystallises from ether–light petroleum in well-developed prisms, m. p. 99°, $[\alpha]_D^{15°} - 6·7°$ in chloroform ($c = 3·0$).

Action of Nitrous Acid on d-neo*Menthylamine and* d-neoiso-*Menthylamine.*—1. *d-neo*Menthylamine hydrochloride (50 g.), obtained by hydrolysing form-*d-neo*menthylamide (m. p. 114—116°), was treated with nitrous acid in the usual manner (this vol., p. 1280). The product contained tarry matter. When distilled it yielded a first fraction (16 g.) having b. p. 57—83°/11 mm., $[\alpha]_D^{15°} + 58·6°$ (in ether; $c = 1·8$), $n_D^{15°}$ 1·4555, and a second fraction (4·2 g.) having b. p. 83—102°/11 mm., $\alpha_D^{15°} - 18·12°$, $[\alpha]_D^{15°} - 20·1°$, $n_D^{15°}$ 1·4630. The latter fraction had an odour of menthol; when heated with phthalic anhydride, it yielded a product which, after two recrystallisations from light petroleum containing a little alcohol, had m. p. 111°, $[\alpha]_D^{15°} - 81·5°$ (in chloroform; $c = 2·1$). A mixture of this substance with *l*-menthyl hydrogen phthalate (m. p. 112—113°) melted at 111—113°; it was therefore diagnosed as slightly impure *l*-menthyl hydrogen phthalate (compare Pickard and Littlebury, J., 1912, **101**, 109).

2. *d-neoiso*Menthylamine hydrochloride (6 g.) was treated similarly, a little dilute hydrochloric acid being added during the progress of the reaction. The crude product (3 g.) when distilled yielded a first fraction (2·1 g.) having b. p. 76—109°/21 mm., $\alpha_D^{15°} + 17·64°$, $n_D^{15°}$ 1·4591, and a second fraction (0·6 g.) having b. p. 90—100°/9 mm., $[\alpha]_D^{15°} + 5·5°$ (in alcohol; $c = 3·7$), $n_D^{15°}$

1·4675. The second fraction, which showed no tendency to crystallise, possessed an odour of *iso*menthol (this vol., p. 1280).

Phototropy of Salicylidenementhylamines.

Of the twelve possible stereoisomeric salicylidenementhylamines, nine have now been described, the remaining three being the derivatives of *d*-menthylamine, *l-neoiso*menthylamine, and *dl-neoiso*menthylamine. The nine stereoisomerides are all normally pale yellow in colour, but it is remarkable that certain of them display phototropy, while the others do not. When exposed for a few minutes to sunlight or to bright daylight, salicylidene-*l*-menthylamine assumes a deep orange colour, but reverts to pale yellow when kept for a while in subdued daylight or in the dark. A less pronounced change of a similar kind is exhibited by the three salicylidene*iso*menthylamines, and to a slight extent by salicylidene-*dl*-menthylamine, but the three salicylidene*neo*menthylamines and salicylidene-*d-neoiso*menthylamine are unaffected by the treatment indicated. Salicylidene-*dl*-menthylamine was originally obtained as a liquid (J., 1926, 2227), but when kept for several months it changed to a pale yellow, crystalline mass, which softened at 60° and melted indefinitely at about 80°. It is hoped in due course to undertake a more detailed study of the phototropy of these derivatives.

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CCXC.—*Reactions of Sodium Compounds of Aromatic Ketones. Part I. Synthesis of Triarylcarbinols and of Triarylmethane Dyes.*

By ERNEST HARRY RODD and FRANK WILLIAM LINCH.

IT has been known for many years that aromatic ketones form compounds with metallic sodium in an inert solvent. The literature of the subject, from the original observation by Beckmann and Paul (*Annalen*, 1891, **266**, 1) that benzophenone forms a coloured compound with sodium, is usefully summarised in *Ann. Reports*, 1925, **22**, 123—126. Workers in this field have hitherto confined themselves to unsubstituted ketones such as benzophenone and phenyl diphenylyl ketone, and have studied the decomposition

products of the sodium ketyls with water, oxygen, iodine, and methyl iodide with the object of elucidating their structure. Schlenk and his co-workers state that benzophenone forms a blue monosodio-derivative, probably containing tervalent carbon, and a violet disodio-derivative, $CPh_2(ONa)Na$; the disodio-compound of phenyl diphenylyl ketone was actually isolated (*Ber.*, 1914, **47**, 487).

We were attracted by the possibility of preparing triarylmethane dyes by the interaction of the sodio-derivatives of suitably substituted ketones with halogenated aromatic compounds. The observation by Frey (*Ber.*, 1895, **28**, 2514), that triphenylcarbinol is formed from benzophenone and bromobenzene in ether in the presence of sodium, made the project appear feasible. Blicke had also observed the formation of triphenylcarbinol from benzaldehyde, bromobenzene, and sodium, and he assumed the intermediate formation of benzophenone (*J. Amer. Chem. Soc.*, 1924, **46**, 2560).

Experiments at once showed that Michler's ketone, *pp'*-tetramethyldiaminobenzophenone, when heated with chlorobenzene in the presence of sodium, gave, after treatment of the product with water, the expected carbinol, which was readily converted into the well-known dyestuff, malachite green. The formation of the sodio-compound of the ketone is extremely slow in ether on account of the low solubility of the ketone and the low b. p. of the solvent, but in benzene or toluene at 80—100° the reaction is much more rapid, and these solvents are suitable for carrying out the synthesis. The reaction has been extended to a number of chlorinated hydrocarbons, including *o*-chlorotoluene, 4-chloro-*m*-xylene, chloro-*p*-xylene, α- and β-chloronaphthalene, and chloroanisoles. In place of Michler's ketone, *pp'*-tetraethyldiaminobenzophenone has been used; with chlorobenzene, this gives the carbinol corresponding with the dye, brilliant green. The condensation of the ketone with the chloro-compound requires two atoms of sodium per mol. of ketone for its completion; by the use of this proportion, with a slight excess of chloro-compound, there is little unchanged ketone and no sodium left at the end of the reaction. The reaction may therefore be expressed by the equations:

$$R_2CO + 2Na = R_2C(ONa)Na;$$
$$R_2C(ONa)Na + R'Cl = R_2R'C(ONa) + NaCl.$$

From our subsequent study of the ketyl compound, however, it is doubtful whether there is ever present any appreciable concentration of the disodio-compound (see following paper).

By means of this reaction several new dyes, not hitherto described because not readily obtainable by known methods, have been prepared. The yields are generally substantial; the carbinols

obtained have in some instances been difficult to purify, whilst in other instances good yields of the pure triarylcarbinol were readily obtained. The yield and quality of carbinol obtained vary with the reaction conditions and with the mobility of the reacting chlorine atom. As by-products, diaryls may be formed by the reaction $2RCl + 2Na = R{\cdot}R + 2NaCl$. On the other hand, the ketyl compound may undergo decomposition with formation of by-products, and may even react with toluene when this is used as solvent. The decomposition of the ketyl compound and its reactions will be discussed in Part II (following paper).

Attempts have been made to obtain dye-bases by heating the ketyl compounds with many other benzenoid chloro-compounds. The presence of groups which may be attacked by sodium, such as nitro- and amino-groups, is always inimical to the reaction. Dichloro-compounds, such as *p*-dichlorobenzene and 4 : 4′-dichlorodiphenyl, gave dye-bases, but difficulty was experienced in purifying them; whilst more highly chlorinated compounds, such as tetrachlorotoluene, only gave traces of dye-base, under the conditions used.

In purifying some of the carbinols obtained, it was observed that, when the dye salts were basified with ammonia, the basified product had an abnormally high nitrogen content. It was eventually proved that basification with ammonia gave, not the carbinol, but the corresponding amine, *e.g.*, $C(NH_2)(C_6H_4{\cdot}NMe_2)_2(C_6H_4Me)$. A similar observation has been made by Noelting and Saas (*Ber.*, 1913, **46**, 953), who obtained the amine $C(NH_2)(C_6H_4{\cdot}NMe_2)_3$ by the action of ammonia on an aqueous solution of crystal violet.

Experimental.

pp′-*Tetramethyldiaminodiphenyl*-o-*tolylcarbinol*, $[(CH_3)_2N{\cdot}C_6H_4]_2C(OH){\cdot}C_6H_4{\cdot}CH_3$.—A mixture of 13·4 g. of *pp*′-tetramethyldiaminobenzophenone, 2·3 g. of sodium, 7 g. of *o*-chlorotoluene, and 50 c.c. of dry toluene was heated in a closed flask provided with a stirrer at 100—105° for 16 hours. The ketone dissolved to a pale yellow solution, but as the reaction proceeded the mixture darkened and a light brown, crystalline powder gradually separated. A little water was added to the reaction mixture, and the toluene and any excess of *o*-chlorotoluene were removed by steam-distillation. The brown, gummy residue of impure carbinol became semi-solid on standing. From the aqueous liquor, a small quantity of *p*-dimethylaminobenzoic acid was obtained by neutralisation with acetic acid. The crude carbinol was extracted with ligroin, filtered from insoluble residue, and the solution evaporated. The carbinol so obtained was dissolved in 100 c.c. of boiling 10% oxalic acid solution and filtered from in-

soluble matter. The oxalate separated on cooling in green, bronzy crystals. These were redissolved in 100 c.c. of hot water and a further amount of insoluble matter was filtered off. This latter contained a little unchanged Michler's ketone. The residue left when the crude carbinol was extracted with ligroin consisted mainly of a product crystallising from toluene in colourless needles, m. p. 190°, which has been identified as *pp'*-tetramethyldiaminodiphenylbenzylcarbinol, $[(CH_3)_2N\cdot C_6H_4]_2C(OH)\cdot CH_2\cdot C_6H_5$. The mode of formation and properties of this substance will be discussed in Part II. The solution of the oxalate of the carbinol was basified with excess of sodium hydroxide. The blue precipitate of pp'-*tetramethyldiaminodiphenyl*-o-*tolylcarbinol* was filtered, washed, dried, boiled out with ligroin, and recrystallised from alcohol. It forms small colourless needles, m. p. 132·5°, becoming light blue on exposure to air. Yield, 8 g. (Found : N, 7·8. $C_{24}H_{28}N_2O$ requires N, 7·8%). The carbinol is moderately soluble in the cold in the usual organic solvents, and readily soluble in warm alcohol and toluene.

When the oxalate is basified with ammonia, pp'-*tetramethyldiaminodiphenyl*-o-*tolylmethylamine* is obtained, which, when recrystallised from ligroin–toluene, has m. p. 163° (Found : N, 11·7. $C_{24}H_{29}N_3$ requires N, 11·7%).

In concentrated sulphuric or hydrochloric acid, the carbinol gives a reddish-brown solution which turns green on addition of water, finally changing to blue. The oxalate gives an intense blue solution in water and a greenish-blue solution in alcohol. Aqueous solutions of the salts of the carbinol dye tannin-mordanted cotton greenish-blue.

Reduction of the carbinol with zinc and 2*N*-hydrochloric acid gave *pp'*-tetramethyldiaminodiphenyl-*o*-tolylmethane, white, glistening needles from alcohol, m. p. 102° (compare Noelting and Gerlinger, *Ber.*, 1906, **39**, 2042).

4-Chloro-*m*-xylene condenses similarly with Michler's ketone to give pp'-*tetramethyldiaminodiphenyl*-m-4-*xylylcarbinol*. This base crystallises from alcohol in small, colourless needles, m. p. 145°.

pp'-*Tetramethyldiaminodiphenyl*-p-*anisylcarbinol*,

$$(NMe_2\cdot C_6H_4)_2C(OH)\cdot C_6H_4\cdot OMe.$$

—A mixture of 13·4 g. of Michler's ketone, 2·3 g. of sodium, 7·5 g. of *p*-chloroanisole, and 50 c.c. of toluene was heated in a boiling water-bath for 12—16 hours in a closed flask with a stirrer. The crude carbinol, obtained by treating the product with water and removing toluene by steam-distillation, was converted into the *oxalate*, which crystallised in bronzy nodules. These were redissolved in hot water, filtered from a little ketone, and the solution was basified with ammonia; the bluish-white *carbinol* was filtered off, washed with a little alcohol, and dried. It separated from ligroin partly as a

gum and partly as crystals; yield, 5·8 g. The latter crystallised from benzene–ligroin in almost colourless needles, m. p. 153° (Found: C, 76·6; H, 7·4; N, 7·5. $C_{24}H_{28}O_2N_2$ requires C, 76·6; H, 7·4; N, 7·4%). The carbinol dissolves in organic acids, *e.g.*, oxalic and acetic acids, to give intense green solutions. Mineral acids give brown solutions turning green on dilution with water. Solutions of the salts dye tannin-mordanted cotton greenish-blue.

pp′-*Tetramethyldiaminodiphenyl*-β-*naphthylcarbinol*.—A mixture of 6·7 g. of Michler's ketone, 1·2 g. of sodium, 4·5 g. of β-chloronaphthalene, and 30 c.c. of dry toluene was stirred for 4½ hours in a boiling water-bath. A dark-coloured product separated during the heating, and on cooling, a copious, grey, crystalline deposit was obtained. This was filtered, washed with a little toluene, and warmed with water; the crude carbinol then remained as a yellow, crystalline powder. The main impurities are unchanged ketone, β-chloronaphthalene, and an appreciable amount of ββ-dinaphthyl. The crude carbinol was purified by conversion into the crystalline oxalate and basification with ammonia; yield, 4·1 g. The *carbinol* crystallises best from aqueous pyridine (in needles) or from benzene–ligroin (in prisms), m. p. 181° (Found: N, 7·0. $C_{27}H_{28}N_2O$ requires N, 7·1%).

pp′-*Tetraethyldiaminodiphenyl*-β-*naphthylcarbinol*.—The reaction proceeds similarly with equivalent amounts of tetraethyldiaminobenzophenone, β-chloronaphthalene, and sodium. In this case the carbinol is easy to purify owing to its sparing solubility in hot alcohol, the impurities being readily soluble. The alcohol-extracted *carbinol*, recrystallised from benzene–ligroin, forms colourless plates, m. p. 177° (Found: N, 6·2. $C_{31}H_{36}N_2O$ requires N, 6·2%). Yield, 51%. The carbinol forms green salts with acids, and aqueous solutions of such salts dye tannin-mordanted cotton a bright yellowish-green.

pp′-*Tetramethyldiaminodiphenyl*-α-*naphthylcarbinol*.—This carbinol is obtained when α-chloronaphthalene is heated with Michler's ketone and sodium. Owing to the greater reactivity of the α-chlorine atom, a much larger proportion of αα-dinaphthyl is formed and this product collects in the portion insoluble in oxalic acid. The crude carbinol is best purified by solution in hot toluene and partial precipitation with ligroin. pp′-*Tetramethyldiaminodiphenyl*-α-*naphthylcarbinol* crystallises from acetone in colourless needles, m. p. 167° (Found: N, 7·0. $C_{27}H_{28}N_2O$ requires N, 7·1%). pp′-*Tetramethyldiaminodiphenyl*-α-*naphthylmethylamine*, obtained by basifying the oxalate with ammonia, has m. p. 186° (Found: N, 10·3. $C_{27}H_{29}N_3$ requires N, 10·6%).

BLACKLEY, MANCHESTER. [*Received, June 8th*, 1927.]

CCXCI.—*Reactions of Sodium Compounds of Aromatic Ketones. Part II. Their Reaction with Methyl and Methylene Groups and their Products of Decomposition.*

By Ernest Harry Rodd and Frank William Linch.

In the preceding paper, it was shown that Michler's ketone and its ethyl homologue combine with sodium in an indifferent solvent to form ketyl compounds which react with aryl chlorides to form triarylcarbinols. Further examination of these ketyl compounds has shown that they are remarkably reactive and that by their means syntheses of a hitherto unrecorded type can be effected. In the course of experiments on the action of sodium on Michler's ketone in toluene solution, a product was obtained in considerable quantity which was eventually proved to be *pp'*-tetramethyldiaminodiphenylbenzylcarbinol, and could only have been produced by the action of the ketyl compound on the methyl group of the toluene. This compound was found to be identical with that obtained as a by-product in the preparation of a triarylcarbinol from Michler's ketone and *o*-chlorotoluene by the action of sodium in toluene solution (Part I). Further experiments showed that the ketyl compound readily reacts with methyl and methylene groups which are generally only attacked by powerful oxidising agents. By this reaction we have been able to prepare with facility a number of new compounds which would be obtainable by known methods only with considerable difficulty.

The Reaction between Michler's Ketone and Toluene in the Presence of Sodium.—It has been shown by previous workers (see Part I) that benzophenone and other aromatic ketones form disodio-compounds, $CR_2(ONa)Na$. If a similar compound were formed by Michler's ketone, it should give, when decomposed by water, Michler's hydrol (tetramethyldiaminobenzhydrol). We attempted to prepare the hydrol by heating Michler's ketone in toluene solution with two atomic proportions of sodium, and obtained, besides the expected hydrol and other by-products which will be discussed later, a considerable yield of pp'-*tetramethyldiaminodiphenylbenzylcarbinol* (I). When benzene was used as solvent instead of toluene, no trace of this compound was formed.

The evidence for the constitution of the compound is as follows. Analysis indicated the formula $C_{24}H_{28}ON_2$, and a molecular-weight determination in camphor gave 350 (calc., 360). The compound shows the properties of a colour base, giving deep blue solutions when dissolved in dilute mineral or acetic acids, but when the solution is

heated the colour disappears. This colour change is due to the formation of a new base having the composition $C_{24}H_{26}N_2$, which has been identified as ββ-*tetramethyldiaminodiphenylstyrene* (II), m. p. 135°. The new base is evidently formed from the first by the loss of the elements of water, and since salt formation first occurs, the formation of the styrene may be represented thus:

$$\underset{\text{(I.)}}{CH_2Ph\cdot C(OH)<\begin{matrix}C_6H_4\cdot NMe_2\\C_6H_4\cdot NMe_2\end{matrix}} \xrightarrow{HCl} \underset{\text{(Blue.)}}{CH_2Ph\cdot C<\begin{matrix}C_6H_4{:}NMe_2Cl\\C_6H_4\cdot NMe_2\end{matrix}}$$

$$\xrightarrow{\text{on heating}} \underset{\text{(Colourless.)}}{CHPh{:}C<\begin{matrix}C_6H_4\cdot NMe_2,HCl\\C_6H_4\cdot NMe_2\end{matrix}} \text{(II.)}$$

By oxidation of the tetramethyldiaminodiphenylbenzylcarbinol with lead peroxide in dilute hydrochloric acid in the cold, phenylacetic acid is obtained, whilst oxidation of the styrene compound readily gives first a greenish-blue dyestuff and then benzaldehyde. The styrene compound is stable to boiling alcoholic potassium hydroxide, but when fused with potassium hydroxide it gives Michler's ketone. All these reactions confirm the constitutions assigned to the two new bases.

The conversion of the carbinol into the styrene derivative is best effected by boiling it for a short time with 10% hydrochloric acid; when the solution is cooled the styrene separates as a sparingly soluble, white, crystalline *dihydrochloride*. This property facilitates the detection of the carbinol and the purification of the styrene. The dihydrochloride is hydrolysed by water with precipitation of the base. A characteristic property of this styrene, and of other similar compounds which we have made, is its oxidation in acetic or dilute mineral acid to an intense blue dyestuff by chromic acid or lead peroxide. The fact that solutions of the carbinol prepared in the cold do not give this reaction but that they give it after heating shows that the conversion of the carbinol into the styrene does not proceed readily in the cold. The cold oxidation of the carbinol to phenylacetic acid illustrates the same point.

When the identity of the product obained from toluene had been established, experiments were extended, and it was found that *p*-xylene gave a similar product with Michler's ketone, whilst tetraethyldiaminobenzophenone reacted similarly with toluene in the presence of sodium.

Reaction with Substances containing the Methylene Group.—Regarding the formation of a benzyl derivative from toluene as due to oxidation of the methyl group with simultaneous formation of benzhydrol, we considered that a substance containing a readily oxidisable methylene group should also react with the sodium

derivative of Michler's ketone. As a convenient substance with which to experiment we chose *pp'*-tetramethyldiaminodiphenylmethane. When this was heated with Michler's ketone and sodium in benzene solution, we obtained without difficulty a good yield of *octamethyltetra-aminotetraphenylethanol*,

$$(NMe_2 \cdot C_6H_4)_2C(OH) \cdot CH(C_6H_4 \cdot NMe_2)_2 \text{ (III)},$$

which by dehydration with sulphuric acid gave octamethyltetra-aminotetraphenylethylene, which has been described by Gattermann (*Ber.*, 1895, **28**, 2876) and Willstätter and Goldmann (*Ber.*, 1906, **39**, 3765). This observation confirmed our conclusions with regard to the reaction products from toluene, and suggested that the reaction might be of general application. To obtain further confirmatory evidence, carbinols were prepared from (*a*) Michler's ketone and tetraethyldiaminodiphenylmethane, and (*b*) tetraethyldiaminobenzophenone and tetramethyldiaminodiphenylmethane, and the two carbinols, $(NMe_2 \cdot C_6H_4)_2C(OH) \cdot CH(C_6H_4 \cdot NEt_2)_2$ (IV) and $(NEt_2 \cdot C_6H_4)_2C(OH) \cdot CH(C_6H_4 \cdot NMe_2)_2$ (V) were shown to give the same ethylene compound by dehydration with sulphuric acid.

Other substances of diverse character containing the methylene group, which have been found to react with the ketyl compound, are acenaphthene and fluorene. In each case, the expected compound was obtained without difficulty in benzene solution. Tetrahydronaphthalene, however, failed to react.

Decomposition Products of the Sodium Ketyl Compound and the Mechanism of its Reaction with Methyl and Methylene Groups.—To explain the ready attack of the ketyl compound on methyl and methylene groups, it is simplest to assume that the radicals $CR_2(ONa)\cdot$ (where $R = NMe_2 \cdot C_6H_4$) are the active agents. Since Michler's hydrol is always a product, the reaction, in the case of toluene, assumes the form $2CR_2(ONa)\cdot + CH_3Ph = CR_2H(ONa) + CR_2(ONa) \cdot CH_2Ph$. For this reaction, only one atom of sodium should be required per mol. of ketone, but when only one atomic proportion of sodium was heated with the ketone in toluene solution, although in the course of 2 hours the whole of the sodium had disappeared, yet no benzyl compound was formed. This observation led us to make a more careful study of the reaction.

With 0·95 atomic proportion of sodium, in two experiments, after heating in a closed vessel for 2 hours and 16 hours, respectively, identical results were obtained: no benzyl carbinol was found, about one-third of the ketone was recovered, and the products included about 0·1 mol. of Michler's hydrol, 0·2 mol. of dimethylaminobenzoic acid, and other bases, including much crystal violet. These, together with dimethylaniline, are the usual products under similar conditions.

When the sodium is increased to 1·5 atomic proportions, a maximum yield of benzylcarbinol is obtained, and sodium remains unchanged at the end; no ketone is recovered. The same result is obtained by using 2 atomic proportions of sodium. A typical experiment, with 1 mol. of Michler's ketone, gave approximately 0·37 mol. of tetramethyldiaminodiphenylbenzylcarbinol, 0·30 mol. of hydrol, 0·08 mol. of dimethylaminobenzoic acid, and 0·11 mol. of colour base.

When benzene is used as solvent, with 2 atoms of sodium, the principal product is Michler's hydrol, with a fair amount of colour base.

During the reaction, the solution gradually assumes an intensely greenish-blue colour, but if air is passed through the apparatus, no blue colour is produced, no hydrol is obtained, and most of the ketone is recovered unchanged, but some dimethylaminobenzoic acid and crystal violet are formed, together with a much redder dyestuff, probably indicating oxidation of the dimethylamino-groups of crystal violet.

If a chloro-compound is added to the reaction mixture, when only one atomic proportion of sodium or less is used, no blue colour appears, but the formation of dye base proceeds at once (*e.g.*, of malachite green, from chlorobenzene), and only traces of the above by-products are formed.

Whilst we feel that more data are required before an entirely satisfactory explanation can be given of all the above observations, we put forward the following discussion tentatively. First, with regard to the colour of the solution obtained when sodium dissolves in a solution of the ketone, it has been freely assumed by Schlenk that free radicals of the type $R_2C(ONa)\cdot$ are coloured, just as Gomberg assumes that free radicals, $R_3C\cdot$, have colour. If this assumption be accepted, then free radicals must always be present in our toluene solutions of the ketyl compound at all stages of the reaction, but the quantity of free radical present may be very small, since traces of oxygen rapidly decolorise the solution. In the presence of a chloro-compound, no colour ever appears, and since the formation of a triarylcarbinol starts at once, it is probably the monosodio-derivative of the ketone which attacks the chloro-compound, as suggested by Schlenk and Weickel to explain the action between sodiobis-diphenylyl ketone and methyl iodide (*Ber.*, 1911, **44**, 1182):

$$2R_2C(ONa)\cdot + R'Cl \begin{cases} \longrightarrow R_2R'C(ONa) \xrightarrow{H_2O} R_2R'C(OH) \\ \longrightarrow R_2CCl(ONa) \longrightarrow R_2CO + NaCl \end{cases}$$

It is not necessary then to assume the formation of a disodio-compound of the ketone (compare Part I).

The non-formation of benzyl compound when only one atom of sodium is used may be due to the greater tendency of a monosodio-radical to combine with another mol. of ketone than to attack a methyl group. We suggest that an intermediate compound, probably of the type $R_2C(ONa)\cdot O\cdot CR_2Na$, is formed,* combination taking place through the oxygen atom, rather than between two carbon atoms. It has been shown recently by Schorigen (*Ber.*, 1926, **59**, 2510) that when sodium acts on complex ethers the point of attack is the oxygen atom. Hence, when more than one atomic proportion of sodium is available, the intermediate compound would be attacked with formation of active free radicals which would attack the toluene :

$$\begin{array}{l} R_2C(ONa)- \\ +C_6H_5\cdot CH_2- \end{array}\!\!\begin{array}{|l} \!\!-\!\!-\!\!-\!\!-O \\ \!\!-H\ \ CR_2Na \end{array} + Na \longrightarrow \begin{array}{l} R_2C\!-\!ONa \\ C_6H_5\cdot CH_2 \end{array} + \begin{array}{l} ONa \\ HCR_2 \end{array} + Na$$

It would appear that the additional sodium acts catalytically, and this agrees with the experimental results, as far as we can interpret them. Owing to side reactions, however, it has not been possible to determine how much of the sodium employed takes part in this reaction.

The observation that oxygen destroys the blue colour formed by the addition of sodium to the ketone, mainly with re-formation of the ketone, agrees with Schlenk's observations on simple aromatic ketones (*Ber.*, 1914, **47**, 487) :

$$2R_2C(ONa)\cdot + O_2 \longrightarrow R_2C(ONa)\cdot O\cdot O\cdot CR_2(ONa) \longrightarrow 2R_2C{:}O + Na_2O_2.$$

The formation of *p*-dimethylaminobenzoic acid, crystal-violet base, and dimethylaniline as by-products must be attributed to a general loosening of the bonds between the aryl radicals and the keto-carbon atom in the ketyl compound. Since these products are formed to the greatest extent when there is a deficiency of sodium, they are probably the result of internal rearrangement in a complex molecule or radical, *e.g.*, $CR_2(ONa)\cdot O\cdot CR_2\cdot \longrightarrow \cdot CR(ONa)\cdot O\cdot CR_3 \xrightarrow{+R_2CO} R_2CNa\cdot O\cdot CR(ONa)\cdot O\cdot CR_3$. The last complex on hydrolysis should give 1 mol. each of Michler's hydrol, dimethylaminobenzoic acid, and crystal-violet base. Undoubtedly we have not yet identified all the by-products, so it is not possible to give a complete picture of the changes taking place. We do not exclude the possibility of the formation of the pinacol, $R_2C(ONa)\cdot CR_2(ONa)$, but we have as yet no evidence for it.

* This type of intermediate compound was also suggested by Beckmann and Paul (*Annalen*, 1891, **266**, 1) to explain the formation of benzophenone and benzhydrol from the monosodio-derivative of benzophenone.

Experimental.

The Michler's ketone used for these experiments was the technical product, purified by boiling with very dilute hydrochloric acid and recrystallising the insoluble portion from alcohol. The toluene used was the commercial product, redistilled and dried over sodium.

pp′-*Tetramethyldiaminodiphenylbenzylcarbinol* (I).—In a flask fitted with a sealed stirrer and a reflux condenser were placed 800 c.c. of toluene, 268 g. of Michler's ketone and 46 g. of sodium, and the whole was heated in a bath kept at 100—105° for 12 hours, with continuous stirring. During the heating, the colour of the solution became deep greenish-blue and remained so throughout the experiment. The blue colour is destroyed at once by air. The contents of the flask were cooled, poured off from the unchanged sodium, and treated with ice to hydrolyse the sodium compounds. The whole was then steam-distilled to remove the toluene and dimethylaniline, if any. The bases were filtered from the alkaline aqueous liquor and extracted thoroughly with ether. The residue consisted of nearly pure pp′-*tetramethyldiaminodiphenylbenzylcarbinol*, 131 g., m. p. 185°. (In those experiments in which only 0·95 mol. of sodium is used, the residue at this stage consists of nearly pure unchanged ketone, which is also almost insoluble in ether.) A similar experiment gave 36 g., m. p. 187°, from 67 g. of Michler's ketone. By recrystallisation from toluene the base is obtained in colourless, transparent needles, often pointed at one end only, m. p. 190·5° (Found: C, 79·62; H, 7·79; N, 7·72; *M*, cryoscopic in camphor, 350. $C_{24}H_{28}ON_2$ requires C, 80·00; H, 7·77; N, 7·77%; *M*, 360). The carbinol dissolves in acetic acid with a blue colour, which becomes intense on warming, then quickly fainter, and finally very pale blue.

The other products of the reaction were separated as follows: The alkaline filtrate obtained above was neutralised to precipitate the *p*-dimethylaminobenzoic acid, which was filtered, dried, and weighed. From the solid residue, consisting of carbinol and other bases, the ether had extracted the latter (see above), and this extract was freed from solvent and dissolved in dilute sulphuric acid. A strong solution of sodium hydrogen sulphite was then added, and the mixture warmed at 60°, whereby the Michler's hydrol was converted into *pp′*-tetramethyldiaminodiphenylmethane-ω-sulphonic acid. The solution was made alkaline with sodium hydroxide, filtered from the precipitated bases, and the sodium ω-sulphonate salted out (when dried, it is approx. 80% pure). The bases were extracted with dilute oxalic acid solution (which left a little ketone in those cases where there was a deficiency of sodium, see p. 2181) and the solution

yielded a considerable amount of crystal violet oxalate. Other bases (unidentified) were, however, also present.

In one experiment, the dimethylaniline in the recovered toluene was found to be 1·4 g. from 67·0 g. of ketone, and the other products, separated as described above, were 27·0 g. of the benzylcarbinol (m. p. 190°, crude), 5·0 g. of dimethylaminobenzoic acid, about 26 g. of Michler's hydrol, and 8·5 g. of crude crystal-violet base.

An experiment was carried out in which the apparatus was sealed with special care and connected to a manometer, after the required temperature had been attained. There was no evidence of any change of pressure, showing that no gaseous products are formed.

ββ-pp′-*Tetramethyldiaminodiphenylstyrene* (II).—This may be prepared from the crude *pp′*-tetramethyldiaminodiphenylbenzylcarbinol by dissolving 20 g. in 100 c.c. of 2*N*-hydrochloric acid and boiling for ½ hour; on cooling, the solution deposits 20 g. of the *dihydrochloride* of the styrene in soft, shining, colourless needles (Found in crude product: Cl, 16·0. $C_{24}H_{28}N_2Cl_2$ requires Cl, 17·1%). The basification is carried out by suspending the hydrochloride in water and gradually stirring in dilute sodium hydroxide. The *base*, recrystallised from a mixture of acetone and methyl alcohol, forms short, pale yellow prisms, m. p. 135° (Found: C, 84·66, 84·21; H, 7·90, 7·92; N, 8·17. $C_{24}H_{26}N_2$ requires C, 84·21; H, 7·60; N, 8·19%). In a quantitative experiment on the conversion of the pure benzylcarbinol into the styrene, 0·7662 g. of the former gave 0·7250 g. of the latter (theory, 0·728 g.).

Oxidation of pp′-*Tetramethyldiaminodiphenylbenzylcarbinol.*—14·4 G. of the carbinol were dissolved in 350 c.c. of cold *N*-hydrochloric acid. A thin paste of 29 g. of lead peroxide was added gradually to the stirred solution of the carbinol and oxidation was allowed to proceed for some hours at the ordinary temperature. The lead was precipitated with sodium sulphate and the filtrate basified with sodium hydroxide. The alkaline solution was extracted with ether, but the basic products of the oxidation could not be obtained sufficiently pure for identification. The solution was then acidified with dilute hydrochloric acid and again extracted with ether. After removal of the ether, an oily residue was left which solidified on standing (5·1 g.). It was recrystallised twice from hot water, giving large, glistening plates, m. p. 76—77°. This product had all the properties of phenylacetic acid, and its identity was established by comparison (mixed m. p.) with a sample prepared from benzyl cyanide.

Octamethyltetra-aminotetraphenylethanol, (III).—A mixture of 26·8 g. of Michler's ketone, 4·6 g. of sodium, 50 g. of *pp′*-tetramethyldiaminodiphenylmethane, and 100 c.c. of dry benzene was heated

at 85—90° for 16 hours with efficient stirring. The sodium was separated and the benzene removed by steam-distillation. The residual white solid was filtered off and boiled out twice with alcohol to remove Michler's hydrol and other impurities. The insoluble white residue (20 g.) was substantially pure *octamethyltetra-aminotetraphenylethanol*. It is sparingly soluble in all neutral organic solvents and is best recrystallised from toluene; colourless needles, m. p. 255° (Found: C, 77·7; H, 8·0; N, 10·7. $C_{34}H_{42}N_4O$ requires C, 78·1; H, 8·0; N, 10·7%). It dissolves in weak mineral acids or glacial acetic acid to give greenish-blue salts which become violet on addition of lead peroxide.

The same method of preparation and the same molecular proportions of materials were used in the following preparations.

αα-4 : 4′-*Tetraethyldiaminodiphenyl*-ββ-4 : 4′-*tetramethyldiaminodiphenylethan*-α-*ol* (V) from *pp*′-tetraethyldiaminobenzophenone and *pp*′-tetramethyldiaminodiphenylmethane: white needles from toluene or alcohol–chloroform, m. p. 228° (Found: N, 9·6. $C_{38}H_{50}N_4O$ requires N, 9·7%).

αα-4 : 4′-*Tetramethyldiaminodiphenyl*-ββ-4 : 4′-*tetraethyldiaminodiphenylethan*-α-*ol* (IV) from *pp*′-tetramethyldiaminobenzophenone and *pp*′-tetraethyldiaminodiphenylmethane: white needles from toluene or alcohol–chloroform, m. p. 229—230° (Found: N, 9·6. $C_{38}H_{50}N_4O$ requires N, 9·7%).

Both compounds dissolve in dilute mineral acids or glacial acetic acid, giving greenish-blue solutions which turn violet on the addition of a little lead peroxide. These ethanol derivatives were converted into the corresponding ethylene compounds by warming with concentrated sulphuric acid.

Octamethyltetra-aminotetraphenylethylene,

$$(NMe_2{\cdot}C_6H_4)_2C{:}C(C_6H_4{\cdot}NMe_2)_2.$$

—5 G. of the ethanol were dissolved in 25 c.c. of concentrated sulphuric acid and warmed for ½ hour in a boiling water-bath. The pale green solution was poured into ice water and the base precipitated by the addition of sodium hydroxide as a yellowish-white powder; yield 4·7 g. It crystallises from acetone–methyl alcohol in greenish-yellow needles, m. p. 314—316° (Gattermann, *Ber.*, 1895, **28**, 2876, gives m. p. 310—315°) (Found: N, 11·1. Calc. for $C_{34}H_{40}N_4$: N, 11·1%). It forms colourless salts when dissolved in acids, but the solutions turn violet on the addition of a little lead peroxide.

αα-4 : 4′-Tetraethyldiaminodiphenyl-ββ-4 : 4′-tetramethyldiaminodiphenylethanol and αα-4 : 4′-tetramethyldiaminodiphenyl-ββ-4 : 4′-tetraethyldiaminodiphenylethanol when warmed with concentrated sulphuric acid gave the same product, *viz.*, αα-4 : 4′-*tetraethyldiaminodiphenyl*-ββ-4 : 4′-*tetramethyldiaminodiphenylethylene*, pale

yellow needles from alcohol–chloroform, m. p. 212°. The identity was established by mixed melting-point and nitrogen determinations (Found: N, 10·0, in each case. $C_{38}H_{48}N_4$ requires N, 10·0%).

4 : 4′-*Tetramethyldiaminodiphenylacenaphthenylcarbinol*, $(NMe_2{\cdot}C_6H_4)_2C(OH){\cdot}C_{12}H_9$.—A well-agitated mixture of 26·8 g. of Michler's ketone, 4·6 g. of sodium, 30 g. of acenaphthene, and 100 c.c. of dry benzene was heated at 85—90° for 16 hours. The excess of sodium was separated and the benzene removed by steam-distillation. The residual crystalline mass was filtered off and boiled several times with alcohol to remove impurities. The white, insoluble residue (12 g.) was recrystallised from toluene; colourless needles, m. p. 232° (Found: N, 6·7. $C_{29}H_{30}ON_2$ requires N, 6·6%). It dissolves in dilute mineral acids or glacial acetic acid to reddish-blue solutions. These solutions are almost decolorised by boiling, and on the addition of a little lead peroxide the resulting solution assumes a violet colour.

4 : 4′-*Tetramethyldiaminodiphenylmethyleneacenaphthene*, $(NMe_2{\cdot}C_6H_4)_2C{:}C_{12}H_8$.—Since concentrated sulphuric acid sulphonates the acenaphthene nucleus, in this case the ethylene derivative was prepared by boiling 5 g. of the ethanol for an hour with aqueous hydrochloric acid. On cooling, a crystalline *hydrochloride* was deposited in fine, white needles. The *base* was obtained as a greenish-yellow powder by basifying with sodium hydroxide. The dried product (4·7 g.) was recrystallised from chloroform–alcohol; pale yellow plates, m. p. 209° (Found: N, 7·0. $C_{29}H_{28}N_2$ requires N, 6·9%). It dissolves in acetic acid to a colourless solution which turns violet on addition of lead peroxide.

4 : 4′-*Tetramethyldiaminodiphenylmethylenefluorene*, $[N(CH_3)_2{\cdot}C_6H_4]_2C{:}C{<}\begin{matrix}C_6H_4\\C_6H_4\end{matrix}$.—A mixture of 13·4 g. of Michler's ketone, 2·3 g. of sodium, 20 g. of fluorene, and 50 c.c. of dry benzene was heated with stirring at 85—90° for 16 hours. The unchanged sodium (0·5 g.) was separated and the benzene removed by steam distillation. The residual, orange, crystalline product was boiled three times with alcohol and the insoluble residue (8·5 g.) was recrystallised first from toluene and finally from chloroform–alcohol; pale yellow needles, m. p. 239—240° (Found: N, 6·7. $C_{30}H_{28}N_2$ requires N, 6·7%). It dissolves in dilute mineral acids or acetic acid to a pale yellowish-green solution which turns blue on addition of lead peroxide. In this case, dehydration of the carbinol to the ethylene derivative has occurred at some stage which has not been determined.

The analyses recorded in Parts I and II were carried out by Mr. W. H. Cliffe, whose help we gratefully acknowledge. The work was carried out in the Research Department of the British Dyestuffs Corporation, Ltd., to whom our thanks are due for permission to publish it.

BLACKLEY, MANCHESTER. [*Received, June 8th*, 1927.]

Addendum.—Since the above work was completed, a paper by Madelung and Völker has appeared (*J. pr. Chem.*, 1927, **115**, 24), in which the formation of *pp'*-tetramethyldiaminodiphenylbenzylcarbinol and of *pp'*-tetramethyldiaminodiphenylstyrene from Michler's ketone and magnesium benzyl chloride is described, the styrene being the principal product. The m. p.'s are stated to be 173° and 129°, respectively, whereas our m. p.'s are 190·5° and 135°. The above authors' compounds are evidently impure, and are most probably contaminated with unchanged ketone, since our observations have shown that with Michler's ketone the Grignard reaction only proceeds to a very limited extent. It is to be noted that earlier workers, by the action of magnesium alkyl halides on Michler's ketone, never obtained carbinols, but always the corresponding ethylene derivative. Madelung and Völker state that the carbinol and the styrene both give the same blue colour in acetic acid (*loc. cit.*, pp. 29, 41). This does not agree with our observations; we find that the former gives a very intense blue colour with cold acetic or with one equiv. of dilute mineral acid, comparable in intensity with the colour given by a true triphenylmethane-dye base, whilst the styrene gives a very weak colour. When the intensely coloured solution of the carbinol in acid is heated, the colour gradually disappears and finally approximates in intensity to that given by the styrene.

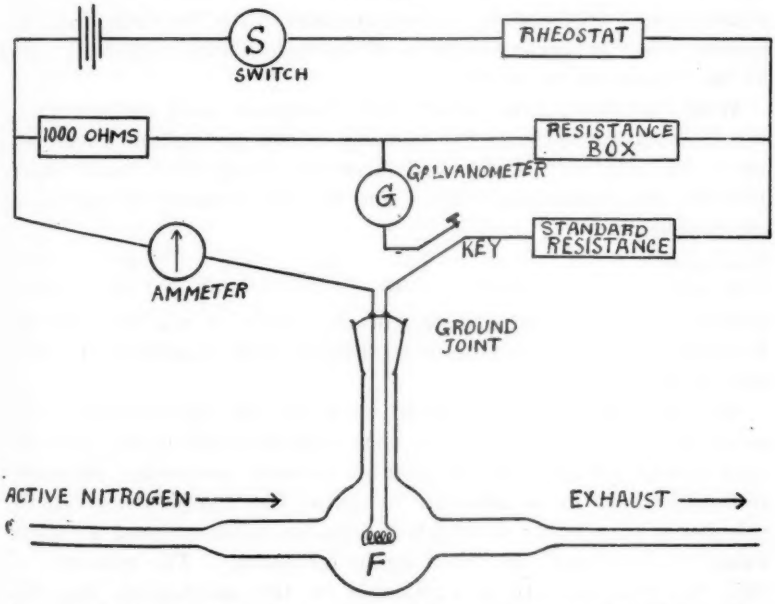
CCXCII.—*On Active Nitrogen. Part III. Active Nitrogen and the Metals.*

By ERIC JOHN BAXTER WILLEY.

WHILST metallic vapours readily combine with active nitrogen to form nitrides (Rayleigh, *Proc. Roy. Soc.*, 1913, *A*, **88**, 539; Willey, *J. Soc. Chem. Ind.*, 1924, **43**, 263), the clean, cold metals rarely exert any noticeable influence upon the afterglow. In ordinary circumstances, copper forms the only exception to this statement, but if mercury or low-melting alloys of lead be employed and the gas be bubbled through the liquid, this rapidly becomes foul and abundant nitride formation occurs, suggesting that the inactivity

of the clean and cold metals is due to the formation of a skin of nitride, which, being inactive, protects the underlying portions of the metal against attack. In view of the fundamental importance of nitride formation in the catalysts employed in the synthesis of ammonia, it was decided to investigate in some detail the effect of active nitrogen on the metals; the results obtained support the foregoing theory, and, moreover, it has been found that in several cases the metals become active catalysts in the destruction of the afterglow at the temperature of decomposition of their nitrides. The experimental data also show that the energy of active nitrogen

FIG. 1.



is *ca.* 45,000 cals./g.-mol., in excellent agreement with the value advanced in earlier communications (J., 1926, 1804; this vol., p. 669), and that the decay process is probably bimolecular with respect to the active nitrogen.

EXPERIMENTAL.

The apparatus employed is shown in Fig. 1. Active nitrogen, cooled to room temperature by passage down a thin-walled tube, flowed over the filament, F, which served both as a resistance thermometer and as a heating coil. The galvanometer and leads were enclosed in an earthed shield, and an auxiliary electrode, also earthed, was provided between F and the end of the discharge in

order to afford protection from stray discharges; in this way, disturbance of the Wheatstone circuit was avoided. The filament was silver-soldered to heavy copper leads sealed through the ground joint as shown.

It was found that both with a bare platinum filament initially at room temperature and with filaments of other metals, as well as those obtained by electrodeposition of coatings so thin as not appreciably to alter the resistance of the original platinum, a very definite increase in temperature occurred when active nitrogen was drawn through the apparatus; this was least in the case of molybdenum and tungsten, and greatest with smooth-surface copper. No such increase in temperature was observed when the filament was replaced by a thermometer, thus showing that the heating effect is due to the decay of the endothermic active nitrogen at the surface of the metal.

With platinum, iron, silver, zinc, tungsten, and molybdenum, the relationship between the velocity of the gas stream (measured upon an arbitrary scale) and filament temperature was linear between the limits examined. The figures obtained for platinum are typical :

Flow speed	0·0	4·0	6·5	8·5	10·3	12·3
Resistance	1·302	1·313	1·320	1·325	1·330	1·335

(Owing to the limited capacity of the pump, it was not possible to work with flow speeds above 1·5 litres/hour, measured at atmospheric pressure.)

With a copper-coated filament, however, the temperature increment was much greater than that obtained previously and the glow ceased abruptly at the metallic surface; moreover, the curve obtained (Fig. 2) is different in form, the temperature rapidly increasing to a value at which it remains constant over a certain range of flow rate, and then again increasing. The existence of this flat portion, AB, is explicable on the assumption that the maximum destruction of active nitrogen at the surface is reached with a gas-velocity corresponding to the ordinate of A, but that at B the gas-velocity is high enough to set up turbulent motion round the filament, causing increased circulation of the gas and a consequent increase in the number of molecules deactivated by the metal. Support for this view was obtained in two ways. It was noticed that so long as the gas-velocity was not too high, the coating of copper remained intact and the experiments could be repeated as often as desired. Above a gas-velocity corresponding closely with B, however, the point at which the afterglow ceased (initially about 2 m. downstream in such experiments) began to recede rapidly, until after about a minute no afterglow was visible except

for localised patches round the electrodes. When the filament was dismounted, the copper coating was found to have vanished almost entirely, whilst the walls of the bulb had become reddish-brown in colour, just as if they had been " spattered " from a copper cathode. Prolonged treatment of the glass with nitric acid produced no change in its colour, and little or no copper could be detected in solution; but quantitative tests in which a long filament was first plated with copper and then cut in two, one half being used for a colorimetric determination of the copper and the other being subjected to the action of active nitrogen, showed that nearly the whole of the copper lost from the wire could be recovered from the bulb if this were powdered and fused with sodium carbonate. Even with the most rigorous protection against stray discharges, the result was the same, and hence it would appear that the disintegration is due to the evolution of heat at the copper surface owing to the decay of large amounts of active nitrogen thereat, whilst the scattered metal has so strong a catalytic effect as to " poison " the glass.

The nature of the copper surface has a great influence in this connexion. If the plating is spongy, the curve obtained shows only the merest trace of flattening, and the disintegration is rapid even at lower gas velocities than before. This " spattering " effect was still more pronounced when the coating had been prepared *in situ* by the reduction of copper oxide by means of active hydrogen in an auxiliary apparatus, whilst commercial copper wire which had been carefully cleaned did not show it at all. No other metal showed any disintegration.

It seems probable, therefore, that, in the case of other metals, the linear relation between gas-velocity and filament temperature corresponds with the portion of the curve to the left of A (Fig. 2), and that if a sufficiently high flow speed could have been attained, they would have given curves showing a similar flattening. It is possible, upon the basis of the data obtained here, to calculate (i) the relative order of catalytic efficiencies of these metals for the destruction of active nitrogen, and (ii), provided a certain assumption be made, the order of the decay process of active nitrogen.

(i) All other factors remaining constant, the increase in the temperature (ΔT) of a filament will be directly proportional to its area (A) and to the catalytic efficiency of the metal (E), and inversely proportional to its weight (W), *i.e.*, $\Delta T = kAE/W$. Now it was noticed that when a current of active nitrogen was drawn past a copper-coated filament, the glow appeared to be entirely extinguished provided that the flow speed was not too high, and hence we may assume that in these circumstances the whole of the

active nitrogen reaching the surface of the filament was transformed to the inert variety. We may thus calculate the catalytic efficiencies of the various metals employed, relative to copper as unity, as shown in Table I. The measurements were all made with filaments immersed in nitrogen flowing at the rate of 1·5 litres/hr. (measured at *N.T.P.*), the gas being at a pressure of 10 mm. Hg and containing 1·5% of active nitrogen.

TABLE I.

Metal.	100 W.	ΔT.	$A \times 10^4$.	E.
Platinum	0·85	8·0	2·2	0·24
Silver	2·1	12·5	3·9	0·26
Zinc	2·1	12·5	3·9	0·26
Iron	2·0	13·0	3·7	0·27
Copper (smooth)	1·15	36·0	2·8	1·00
Copper (spongy)	1·84	15·0	3·6	0·33
Tungsten	2·3	0·0	—	0·0
Molybdenum	0·8	0·0	—	0·0

(ii) Let us make the very probable assumption that a constant fraction of the active nitrogen present at any instant is decomposed at the filament surface; then, from the linear relation between the flow speed and the temperature increment in the filament, we see that the number of active nitrogen molecules present at any instant varies directly with the flow speed of the gas and therefore inversely as the time (t) taken for a molecule to travel from the discharge to the filament, *i.e.*,

$$[N_2'] = k'/t, \text{ or } -d[N_2']/dt = k'/t^2.$$

Hence the decay process is, upon this assumption, bimolecular with respect to the active nitrogen.

It was hoped to use the results of these experiments in conjunction with the Hertz–Knudsen equation (which provides a means of calculating the number of molecular impacts per unit area per second) to evaluate the energy of active nitrogen. Such attempts, however, did not lead to intelligible results. It was then thought that if the "blanketing" effect of the converted nitrogen round the filament could be eliminated by the use of a hot wire, data of more value might be obtained, for it is obvious that the conditions obtaining near the cold filaments are somewhat complicated. Furthermore, the metals should, *ex hypothesi*, become completely active at or about the temperatures of decomposition of their nitrides, and this view was tested in the next series of experiments.

The temperature of the wire was gradually raised by altering the adjustment of the rheostat, and its resistance was determined for each setting in a stream of inert nitrogen at 10 mm. pressure, a constant flow speed being maintained all the time; the usual

parabolic relationship between current and resistance was obtained, as shown in Figs. 3 A, B, and C. The nitrogen was then activated and the procedure repeated, with the result that in the case of

FIG. 2.

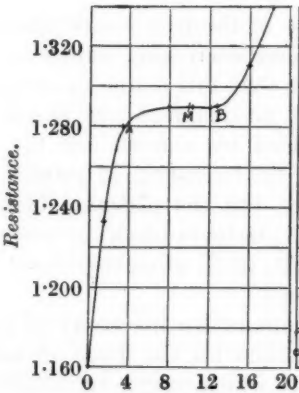


FIG. 3A.
Silver.

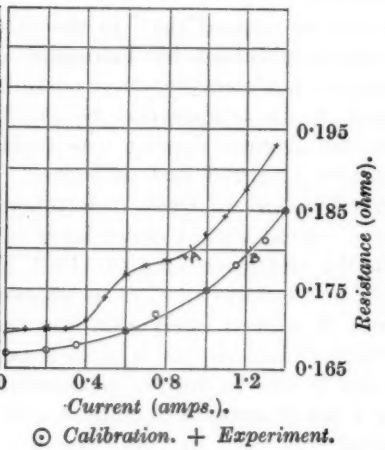


FIG. 3B.
Copper.

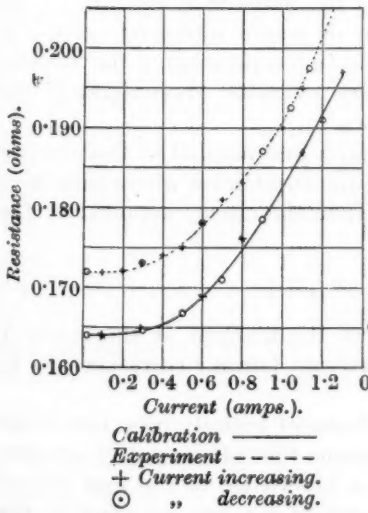
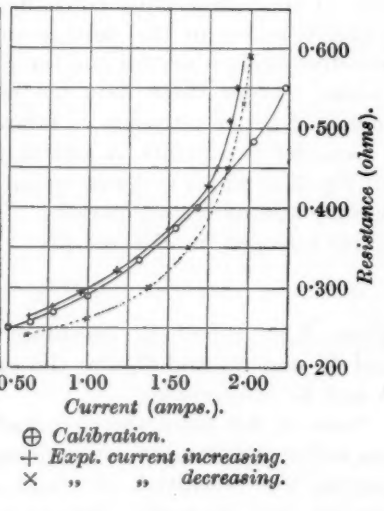


FIG. 3C.
Iron.



iron (Fig. 3 C), platinum, and silver (Fig. 3 A) marked "breaks" were found in the curves, at *ca.* 300°, 92°, and 30°, respectively. Moreover, at these temperatures the glow practically ceased as the

active nitrogen reached the filament, indicating that it was being destroyed by the hot wire. No departure from the calibration curve was noticed with tungsten and molybdenum filaments, but with copper (Fig. 3 B) the form of the curve shows that the section above the break has already been reached even at the ordinary temperature.

It will be noticed that, in the case of the iron-coated filament, the curves obtained for increasing and decreasing values of the current do not coincide; it is possible that this is due to sintering, in view of the temperature to which the filament was raised, for when the original deposit was replaced by a fresh one the discontinuity occurred just as before. No formation of nitride was observed in any of these experiments, but the platinum filament became coated with a dense layer of platinum-black, as observed by Beilby and Henderson (J., 1901, **79**, 1253) when this metal was heated in a current of gaseous ammonia.

Since it seemed likely that the comparative inactivity of commercially drawn copper wire as a catalyst for the decay of active nitrogen is due to surface phenomena which might be minimised when a hot filament is in contact with active nitrogen, the ordinary material was used in this case, with the result, as will now be shown, that complete activity appeared when the hot metal was used. The significance of these breaks in the curves is clearly that at the temperature concerned the filament is becoming catalytically active in the destruction of active nitrogen; energy is therefore being liberated and the rise in temperature of the filament follows. From these data we may evaluate approximately the energy of active nitrogen, as follows.

Consider two points, A and B, on a line parallel to the abscissa (in Fig. 3 A) which is drawn to cut the two curves where they have become approximately parallel. Then the energy supplied by the active nitrogen (in cals./sec.) is

$$R_T(C^2_B - C^2_A)/4{\cdot}2 \quad . \quad . \quad . \quad . \quad . \quad \text{(i)}$$

where R_T is the ohmic resistance of the filament at the points A and B, and C_A and C_B are the currents (amps.) corresponding to A and B, respectively.

Since at this point the glow had almost entirely been lost in the gas below the filament, we may assume that all the active nitrogen passing was destroyed, and from a knowledge of the flow rate of the gas and its active-nitrogen content we can calculate n, the number of molecules undergoing conversion per second. Thus from (i) we have $R_T(C^2_B - C^2_A) = nq$, where q is the energy of a single

molecule of active nitrogen. The energy of active nitrogen per g.-mol., Q, is then given by the expression :

$$Q = R_T(C^2_B - C^2_A) \times 6{\cdot}06 \times 10^{23}/4{\cdot}2n.$$

TABLE II.

Metal.	R_T.	C_A.	C_B.	Flow speed (c.c./hr. at *N.T.P.*)	$n \times 10^{-17}$.	Q.
Platinum ...	0·530	0·45	0·54	1500	1·7	40,200
Silver	0·180	0·92	1·24	3000	3·4	52,700
Copper	0·175	0·48	0·80	2000	2·2	47,000
					Mean	46,600

It will be noticed that if evaluations of Q are made from the two curves just after activity has set in, values much higher than 46,000 cals./g.-mol. are obtained. This is probably due to the "blanketing" effect mentioned on p. 2192, and it was therefore necessary to make calculations from points on the curves corresponding to a sufficiently high temperature to ensure an adequate circulation of the gas, *i.e.*, from points at which the curves are parallel.

It now remains to discuss the probable mode of action of the metals upon active nitrogen. The existence of definite points at which they became active (and in two cases, a definite action of the active nitrogen upon the metal surface) would point to the catalytic decay process being due to the alternate formation and decomposition of the nitride, and the temperatures in question lend a certain measure of support to this view. This is most apparent in the case of iron, since the activity sets in at about 300° and the nitride commences to decompose between 300° and 400° (Baur and Voerman, *Z. physikal. Chem.*, 1905, **52**, 467; White and Kirschbraun, *J. Amer. Chem. Soc.*, 1906, **28**, 1343; Noyes and Smith, *ibid.*, 1921, **43**, 475). The temperatures of decomposition of the corresponding substituted-ammonia compounds of silver, platinum, and copper do not appear to have been determined, although the data of Beilby and Henderson (*loc. cit.*) show that they are comparatively low, and in the absence of evidence to the contrary we may regard this tentative explanation as justified.

Summary.

The catalytic activity of certain metals in the form of fine filaments in accelerating the decay of active nitrogen has been studied both at the ordinary and at higher temperatures. From the data obtained an evaluation of the energy of active nitrogen has been made which agrees well with the value already found, and it appears

that the activity of the metals in this respect probably depends upon the stability of their nitrides; of the metals employed, copper appears to be by far the most active. It has also been shown that the decay process of active nitrogen in the gas phase is bimolecular with respect to the active nitrogen.

The author's acknowledgments are due to Dr. E. K. Rideal for his interest and advice with regard to these experiments.

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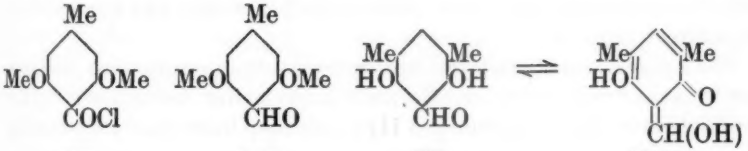
CCXCIII.—*A Synthesis of Pyrylium Salts of Anthocyanidin Type. Part XIV.*

By ALEXANDER ROBERTSON and ROBERT ROBINSON.

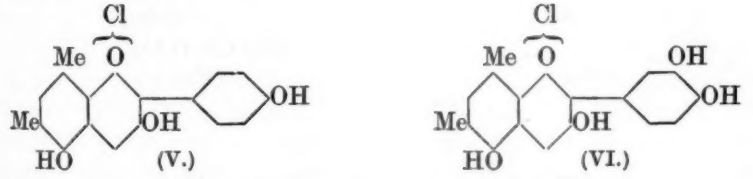
ALL the anthocyanins derived from cyanidin chloride (3 : 5 : 7 : 3′ : 4′-pentahydroxyflavylium chloride) which have been described by Willstätter and his collaborators give a strong ferric chloride reaction, and hence the attachment of the sugar residues to positions 3′ and 4′ is highly improbable. Moreover, we know that the free hydroxyl-group combination (3 : 7 : 3′ : 4′) leads to the exhibition of an alkali colour-reaction practically identical with that due to the combination (3 : 5 : 7 : 3′ : 4′), whilst, on the other hand, the combination (5 : 7 : 3′ : 4′) produces a different effect. The evidence would clearly be much more complete if the effect of the combination (3 : 5 : 3′ : 4′) could be estimated, and the present communication includes a description of flavylium salts containing free hydroxyl groups in these positions. The results may be stated as follows. The combination (3 : 5 : 3′ : 4′) is intermediate between (3 : 7 : 3′ : 4′) and (5 : 7 : 3′ : 4′), and whilst it is closer to the former in one substance, it is closer to the latter in another; thus the influences of small constitutive variations are sufficiently pronounced to diminish the value of the argument from the colour-reactions. The present results are, however, in complete agreement with the conclusions of Pratt and Robinson (J., 1925, **127**, 1131) regarding the constitution of the anthocyanins. In order to obtain 3 : 5 : 3′ : 4′-tetrahydroxyflavylium salts by the usual methods, we required 2 : 6-dihydroxybenzaldehyde or a suitable derivative. The first line of attack was through *p*-orsellinic acid, the method for the preparation of which has been greatly improved. The acid could not be reduced directly by means of sodium amalgam in the presence of boric acid and *p*-toluidine (or sodium bisulphite), although Weil

(*Ber.*, 1922, **55**, 224, 301, 2664) has applied this process with satisfactory results to the reduction of derivatives of salicylic acid. Next, 2 : 6-*dimethoxy*-4-*methylbenzoyl chloride* (I) could not be reduced directly by Rosenmund's method, neither could the *imino-chloride* derived from the related p-*toluidide* be reduced by following the conditions prescribed by Sonn in analogous cases (*Ber.*, 1919, **52**, 1927). The *nitrile* corresponding to (I) could, however, be reduced by an application of the method due to Stephen (J., 1925, **127**, 1874), although the aldehyde (II) was obtained in poor yield and was found to be useless for the special purpose in view. Finally, we succeeded in obtaining a substituted 2 : 6-dihydroxybenzaldehyde, namely, m-*xylorcylaldehyde* (III), by applying the Gattermann synthesis to *m*-xylorcin. The aldehyde is a bright yellow substance, and for this reason it may be best represented by the constitution (IV).



(I.) (II.) (III.) (IV.)

On condensation with ω : 4-dimethoxyacetophenone and ω-methoxyacetoveratrone in formic acid solution under the influence of hydrogen chloride, the *m*-xylorcylaldehyde readily yielded *flavylium* salts which, after demethylation, had the formulæ (V) and (VI), respectively.

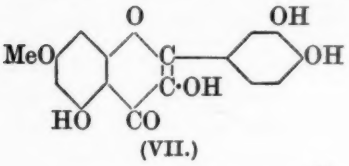


(V.) (VI.)

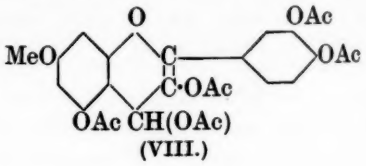
The reactions of (V), taken in conjunction with other similar data, suggest that pelargonin is a pelargonidin 5-diglucoside and callistephin a pelargonidin 3-glucoside, but in view of the problematic effect of the methyl groups, the 7-saccharide configuration is not definitely excluded in either case. The alkali colour-reaction of (VI) is similar to that exhibited by mecocyanin, but the methyl groups may have a reddening influence, as indeed the properties of rhamnetinidin (see below) suggest. A survey of commercial dyestuffs provides no certain guide as to the probable effect on the colour of the substitution of methyl for hydrogen. Thus new magenta is bluer than magenta, but phenosafranine is bluer than

safranine-T, and further conflicting cases could be quoted. In order to obtain a flavylium salt with free hydroxyl groups in the positions 3 : 5 : 3′ : 4′, still more closely related to a cyanidin 7-glucoside, we have reduced the flavonol rhamnetin (VII) to the related *rhamnetinidin chloride* (IX). Rhamnetin is known to be quercetin 7-methyl ether because on fission it yields phloroglucinol monomethyl ether, and on methylation quercetin 3 : 7 : 3′ 4′-tetramethyl ether, the so-called yellow quercetin tetramethyl ether. The specimen employed was derived from xanthorhamnin and was free from quercetin and rhamnazin. The reduction of quercetin to cyanidin chloride was accomplished by Willstätter and Mallison (*Sitzungsber. K. Akad. Wiss. Berlin*, 1914, 769), who employed magnesium as the reducing agent in methyl-alcoholic hydrogen chloride solution; the yield was poor and the product was difficult to isolate. We made many unsuccessful experiments with the object of improving the direct method, and therefore had to resort to an indirect process.

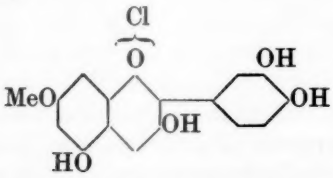
Rhamnetin was acetylated and reduced by zinc dust in boiling acetic anhydride solution (Herzig's acetylating reduction). The product [probably containing (VIII)] was then hydrolysed by means of aqueous-alcoholic hydrochloric acid with formation of rhamnetinidin chloride and other substances. This method constitutes an advance, although the yield of pure product remains unsatisfactory. The insoluble by-products probably arise from a pinacol



(VII.)



(VIII.)



(IX.)

formed in the reduction, and the optimum conditions for the process are being studied in detail in connexion with the reduction of quercetin and kaempferol. The alkali colour-reaction of rhamnetinidin is much closer to that of cyanidin and cyanin than to that of mecocyanin. This is the most definite evidence at our disposal, and it points clearly to the conclusion that mecocyanin, chrysanthenin, asterin, idaein, keracyanin, and prunicyanin are cyanidin 3-saccharides. Similarly, cyanin is indicated as a cyanidin 5-diglucoside,

but we are on less safe ground here, since it is the general experience that purification of an anthocyanidin makes the alkali colour-reaction become bluer and never redder. Whilst, therefore, the fact that rhamnetinidin surpasses mecocyanin in the purity (absence of red) of the blue colour of its alkaline solutions could hardly be explained away as due to impurity of the rhamnetinidin (the presence of cyanidin in significant amount being excluded by the determination of methoxyl content and by the ascertained absence of quercetin in the rhamnetin employed), yet we could not, in view of the circumstances, be sure that further purification would not yield a rhamnetinidin having reactions identical with those of cyanin and cyanidin.

EXPERIMENTAL.

p-Orsellinic Acid and some Derivatives.—The method adopted for the preparation of the acid is based on that by means of which Brunner (*Annalen*, 1907, **357**, 321) obtained γ-resorcylic acid in 40% yield from resorcinol. A mixture of orcinol (20 g.), potassium bicarbonate (40 g.), and glycerol (40 g.) was heated (oil-bath at 115—120°) for 6 hours in an atmosphere of carbon dioxide. The *p*-orsellinic acid (16 g.) isolated from the reaction product is almost pure and, after crystallisation from boiling water (some decomposition to orcinol) and drying at 100°, had m. p. 165—166° (decomp.). The methyl ester has previously been obtained by Herzig (*Monatsh.*, 1903, **24**, 894) by the action of diazomethane on the acid. We have prepared the substance by the action of methyl iodide on silver *p*-orsellinate in boiling benzene solution. It crystallises from light petroleum in elongated, flat prisms, m. p. 93—94° (Herzig gives m. p. 98—99°) (Found: C, 59·4; H, 5·7. Calc. for $C_9H_{10}O_4$: C, 59·4; H, 5·5%). The m. p. could not be raised by repeated crystallisation. The ethyl ester has previously been obtained by Lipp and Schiller (*Ber.*, 1909, **42**, 1967) as a by-product from the condensation of ethyl sodioacetoacetate and propylene dibromide. These authors quote the m. p. 61°; we applied the silver-salt method and our ester crystallised from 60% alcohol in prismatic needles, m. p. 62°. These esters, like *p*-orsellinic acid, give a blue coloration with ferric chloride. [The publication of Wagenhofer on the complete methylation of *p*-orsellinic acid (*Monatsh.*, 1924, **45**, 223) appeared in the course of our work.] The acid (15 g.) was methylated by means of methyl sulphate (58 g.) and aqueous sodium hydroxide, giving methyl *p*-orsellinate dimethyl ether (12 g.). This ester has m. p. 86°, and on hydrolysis yields the acid, m. p. 180—182° (decomp.) (Found: C, 61·5; H, 6·3. Calc. for $C_{10}H_{12}O_4$: C, 61·3; H, 6·1%) (Herzig, *loc. cit.*, gives m. p. 178°).

2 : 4-*Dimethoxy*-6-*methylbenzaldehyde* (*Orcylaldehyde Dimethyl Ether*).—This substance, stated to melt at 62°, has been prepared by Gattermann by nuclear synthesis from orcinol dimethyl ether (*Annalen*, 1907, **357**, 372). We prepared the compound from orcylaldehyde in order to carry out certain confirmations of orientation, and because we were attempting the synthesis of the isomeric *p*-orcylaldehyde dimethyl ether. The methylation of the aldehyde (1 mol.) was effected by means of methyl sulphate (1·5 mol.) and aqueous sodium hydroxide (2 mol.). The alkali-insoluble product crystallised from light petroleum in small, colourless needles, m. p. 64—65°. On oxidation with potassium permanganate, orsellinic acid dimethyl ether was obtained in good yield. This crystallised from 20% acetic acid in glistening prisms, m. p. 143—144° (decomp.) (Found: C, 61·2; H, 6·2. Calc. for $C_{10}H_{12}O_4$: C, 61·3; H, 6·1%). The acid (m. p. given as 140°) has been previously obtained by Herzig (*loc. cit.*) by hydrolysis of the product of methylation of orsellinic acid by diazomethane. A mixture of the dimethyl ethers of orsellinic acid and *p*-orsellinic acid began to melt at 130°.

2 : 6-*Dimethoxy*-4-*methylbenz*-p-*toluidide*.—Phosphorus pentachloride (9 g.) was added to a mixture of *p*-orsellinic acid methyl ether (8 g.) and carbon tetrachloride (or benzene) (50 c.c.), and the reaction completed at 50°. The residue, left after the removal of the solvent and phosphoryl chloride under diminished pressure, was redissolved in benzene (100 c.c.) which was distilled away as before, leaving the 2 : 6-*dimethoxy*-4-*methylbenzoyl chloride* (I) as a mass of colourless needles, m. p. 84—85° (for the purest specimen obtained). The p-*toluidide* was obtained by the action of an excess of *p*-toluidine on a solution of the acid chloride in benzene. It crystallised from benzene, followed by light petroleum, in colourless needles, m. p. 168—169° (Found, in material heated at 100° for 6 hours with loss of benzene: C, 71·7; H, 6·8. $C_{17}H_{19}O_3N$ requires C, 71·6; H, 6·6%). This *p*-toluidide is moderately readily soluble in methyl or ethyl alcohol, and sparingly soluble in benzene or light petroleum. From a suspension of it in benzene (6 g. in 50 c.c.) the corresponding *imino-chloride* was prepared by the action of phosphorus pentachloride (5 g.) for 10 minutes on the steam-bath. After removal of the benzene and phosphoryl chloride, a colourless solid was obtained. On exposure to moist air, this was quickly converted into the original *p*-toluidide, m. p. 168—169°.

2 : 6-*Dimethoxy*-4-*methylbenzamide*, $(MeO)_2C_6H_2Me{\cdot}CO{\cdot}NH_2$.—A stream of ammonia was led through a solution of 2 : 6-dimethoxy-4-methylbenzoyl chloride (10 g.) in benzene (150 c.c.), and the solid which separated was collected, washed with water, and crystallised

from benzene; slender needles, m. p. 199° (yield, 7 g.) (Found: C, 61·5; H, 6·8. $C_{10}H_{13}O_3N$ requires C, 61·5; H, 6·7%). Its solubilities resemble those of the *p*-toluidide.

2 : 6-*Dimethoxy*-4-*methylbenzonitrile*.—A solution of the foregoing amide in pure thionyl chloride was boiled for 5 minutes, and the thionyl chloride then distilled under diminished pressure; the last traces were eliminated by the addition of benzene and redistillation. The *nitrile* (yield, 65—70%) crystallises from benzene–light petroleum in prismatic rods, m. p. 138—139° (Found: C, 68·0; H, 6·5. $C_{10}H_{11}O_2N$ requires C, 67·8; H, 6·2%). The substance may also be crystallised from 60% alcohol in large, squat prisms.

2 : 6-*Dimethoxy*-4-*methylbenzaldehyde* (II).—Hydrogen chloride was led into a mixture of powdered anhydrous stannous chloride (15 g.) and ether (150 c.c.) until a homogeneous solution was obtained. 2 : 6-Dimethoxy-4-methylbenzonitrile (6 g.), dissolved in a little chloroform, was then added, and the passage of hydrogen chloride continued until the liquid was saturated. Crystals separated after 12 hours; after 14 days, the separated solid weighed 8 g. and ultimately about 1 g. more was obtained. This double tin salt crystallised in needles and was very difficult to hydrolyse. The best results were obtained by dissolution in water at 40—50°, addition of an excess of sodium acetate, and heating on the steam-bath for 3 minutes. The *aldehyde* (1·5 g.) was isolated by means of ether, and crystallised from light petroleum in long, colourless, prismatic needles, m. p. 90—91° (mixed m. p. with orcylaldehyde dimethyl ether, 50—55°) (Found: C, 66·7; H, 6·7. $C_{10}H_{12}O_3$ requires C, 66·7; H, 6·7%). This substance is readily soluble in ether and the simple alcohols, moderately readily soluble in benzene, and slightly soluble in hot water. It yields a yellow, sparingly soluble p-*nitrophenylhydrazone* and reduces an ammoniacal silver solution. All attempts to condense it with ω-methoxyacetoveratrone were fruitless, and, no doubt as the result of steric hindrance, it does not appear to form a Schiff's base by condensation with aniline.

4-*Nitro*-6-*hydroxy*-m-*xylene*.—The nitration of *m*-xylidine (100 g.) by the method of Nöelting and Collins (*Ber.*, 1884, **17**, 265) gave 4-nitro-6-amino-*m*-xylene (80 g.), and this was converted into the corresponding phenol by the following method (compare D.R.-PP. 95,339 and 97,012) which is superior to that described by Pfaff (*Ber.*, 1883, **16**, 616). A diazonium salt solution, prepared at below 0° from the nitro-amine (16·6 g.), sulphuric acid (50 g.), crushed ice and water (300—350 g.), and sodium nitrite (7 g.), was filtered and gradually added to boiling 55% sulphuric acid (350 c.c.). On cooling, the nitroxylenol separated in light brown crystals (12—

14 g.), which could be employed for the next stage. The substance crystallised from hydrochloric acid in very slender needles, m. p. 95°. The reduction to 4-amino-6-hydroxy-*m*-xylene (Pfaff, *Ber.*, 1883, **16**, 1137) was conveniently effected by means of iron in alcoholic solution (compare West, J., 1925, **127**, 494). Iron powder (80 g.) was added in portions of about 10 g. at intervals of 3 minutes to a boiling solution of the nitro-*m*-xylenol (55 g.) in alcohol (300 c.c.) and concentrated hydrochloric acid (20 c.c.), and the mixture was boiled for 5 hours, a test then showing that reduction was complete. The filtered solution was concentrated to 100 c.c., cooled, and saturated with hydrogen chloride. After keeping in an ice-chest for some hours, the hydrochloride was collected, and a further quantity could be isolated from the mother-liquor by concentration to 50 c.c. and renewed saturation with hydrogen chloride. The salt crystallised in glistening plates; total yield of practically pure substance, 45 g.

m-*Xylorcin*.—The method of Pfaff (*loc. cit.*) for the preparation of this phenol gave unsatisfactory results, and we adopted the following procedure: 4-Amino-6-hydroxy-*m*-xylene hydrochloride (16 g.) was dissolved in 10% sulphuric acid (200 c.c.) by heating, and crushed ice (200 g.) was added after sudden cooling and shaking to ensure the separation of small crystals. Sodium nitrite (6·4 g.), dissolved in a little water, was then introduced, and the mixture stirred until the sulphate had disappeared. A little charcoal was added, and the diazo-solution filtered and gradually added to 600 c.c. of boiling 10% sulphuric acid. Very little tarry matter was produced, and the filtered solution (charcoal), which was almost colourless, was saturated with ammonium sulphate. Part of the xylorcin crystallised and was collected; the remainder was isolated by six extractions with ether. The product crystallised from benzene in colourless, hexagonal plates, m. p. 124—125° (yield, 8—10 g.). The substance has the properties attributed to it by Pfaff.

m-*Xylorcylaldehyde* (III).—A mixture of *m*-xylorcin (10 g.), anhydrous hydrogen cyanide (15 c.c.), and ether (150 c.c.) was saturated with hydrogen chloride, and the aldimine-hydrochloride separated in almost colourless, prismatic needles in 1 hour. After keeping over-night, the salt was collected, washed with ether, dried, and dissolved in cold water (200 c.c.). The solution was heated at 80—90° for 15 minutes, and a part of the *aldehyde* crystallised, the remainder separating in long, yellow needles on cooling. The substance was recrystallised from 40% ethyl alcohol (charcoal); bright yellow, prismatic needles, m. p. 155—156° (Found: C, 64·8; H, 6·0. $C_9H_{10}O_3$ requires C, 65·1; H, 6·0%). So far as we are able to judge, the striking colour of this substance is not due to

impurity, and Gattermann has noted the yellow colour of 4 : 8- and 2 : 7-dihydroxynaphthaldehyde (Annalen, 1907, **357**, 341).

3 : 4′-*Dimethoxyflavylium Chloride*.—Bright scarlet needles (changing to orange-red on contact with air) separated when hydrogen chloride was passed into a solution of salicylaldehyde (2·2 g.) and ω : 4-dimethoxyacetophenone (3·4 g.) in ether (80 c.c.). The *chloride* recrystallised from 8% hydrochloric acid in glistening, red, prismatic needles (yield, 5·7 g.) (Found, in material dried over sulphuric acid in a high vacuum for 12 hours : C, 60·0; H, 5·7. $C_{17}H_{15}O_3Cl,2H_2O$ requires C, 60·3; H, 5·6%). The substance is sparingly soluble in cold dilute hydrochloric acid, but easily soluble in the hot solvent. The ferrichloride crystallised from acetic acid in small, dull orange, prismatic needles, m. p. 151—152°. Pratt and Robinson described (J., 1923, **123**, 751) hair-fine, orange-red needles, m. p. 135°, so that it is possible that this substance exists in two modifications. The crystalline form, colour, and melting point are different, and in repeating the preparation through the unsaturated ketone we obtained the salt, m. p. 151—152°.

3 : 4′-*Dihydroxyflavylium Chloride*.—This salt is of interest inasmuch as it contains hydroxyl groups in the two positions considered to have the greatest effect on the alkali colour-reactions of the anthocyanidins. Thus, a comparison of the colour of alkaline solutions of this salt and of 7 : 3′ : 4′-trihydroxyflavylium chloride and the representative of the 5 : 3′ : 4′-hydroxylated series described below demonstrates the relatively feeble hypsochromic character of the hydroxyl groups in positions 7 and 5. A mixture of 3 : 4′-dimethoxyflavylium chloride (2·5 g.), phenol (10 g.), and hydriodic acid (60 c.c.; *d* 1·7) was boiled for 30 minutes in an atmosphere of carbon dioxide. After cooling, the phenolic layer was separated, and the demethylated *iodide* was obtained in slender, bright red needles by the addition of ether (yield, 0·7 g.). The *chloride*, obtained in the usual manner by means of silver chloride in methyl-alcoholic solution, was precipitated, after concentration, by dilute hydrochloric acid as a mass of bright red plates, and crystallised from 5—6% hydrochloric acid in red plates exhibiting a golden reflex. Rapid cooling causes the separation of needles (Found, in material dried over soda–lime for 12 hours : C, 59·6; H, 5·1.

$$C_{15}H_{11}O_3Cl,1{\cdot}5H_2O$$

requires C, 59·7; H, 4·7%). The salt crystallises from ethyl-alcoholic hydrogen chloride in flat, pointed prisms. It is moderately soluble in 4—6% hydrochloric acid and very readily soluble in hot dilute or concentrated hydrochloric acid, giving orange to orange-red solutions. When it is treated with much water, a colourless solution of the pseudo-base is obtained, addition of acids

restoring the orange-yellow colour of the flavylium salt. Aqueous or aqueous-alcoholic sodium carbonate dissolves the salt to a red solution, tinged with violet.

5-Hydroxy-3 : 4′-dimethoxy-6 : 8-dimethylflavylium Chloride.—A solution of *m*-xylorcylaldehyde (2 g.) and ω : 4-dimethoxyacetophenone (3 g.) in formic acid (25 c.c.) was saturated with hydrogen chloride, kept for 48 hours, and mixed with an excess of dry ether. The precipitated dark brown, prismatic needles were collected and crystallised from 8% hydrochloric acid as a dark brown, matted mass of slender, woolly needles (3 g.) (Found, in material dried over soda-lime for 12 hours: C, 57·1; H, 6·2. $C_{19}H_{19}O_4Cl,H_2O$ requires C, 57·4; H, 6·3%).

The *ferrichloride* crystallised from acetic acid in spherical aggregates of brown, prismatic needles, m. p. 211—212° after darkening at 190°.

3 : 5 : 4′-Trihydroxy-6 : 8-dimethylflavylium Chloride (V).—The foregoing dimethyl ether (2 g.) was demethylated by boiling hydriodic acid (60 c.c.; *d* 1·7) and phenol (20 g.) in 40 minutes (passage of carbon dioxide). The iodide was precipitated from the separated phenolic layer by means of ether in purple rods (1 g.), and converted into the *chloride* in the usual way. This salt separated from its concentrated aqueous methyl-alcoholic hydrochloric acid solution in violet, prismatic needles, and was recrystallised from 8% hydrochloric acid; glistening, violet needles (Found, in material dried in a high vacuum over sulphuric acid for 24 hours: C, 63·9; H, 5·1. $C_{17}H_{15}O_4Cl$ requires C, 64·1; H, 4·7%). This salt is very sparingly soluble in cold dilute hydrochloric acid but dissolves freely in the hot solvent to a reddish-brown solution. Unlike most flavylium salts, the anhydrous material is not hygroscopic and, as the crystals suffered no change in appearance on drying, it would appear that they separated in the anhydrous condition. The alcoholic solutions are not fluorescent, and on dilution with water give almost colourless solutions of the pseudo-base. The colour of the solution in aqueous sodium carbonate is reddish-violet, and in aqueous-alcoholic sodium carbonate, bluish-violet.

5-Hydroxy-3 : 3′ : 4′-trimethoxy-6 : 8-dimethylflavylium Chloride.—The condensation of *m*-xylorcylaldehyde and ω-methoxyacetoveratrone was carried out as in the analogous case (above) and the yield was almost quantitative. A hot solution of the crude salt in 0·5% hydrochloric acid was filtered, and the acid concentration increased to 8%. The dark red, woolly needles which separated were collected, and when dried exhibited a green reflex. The solutions in hot 7—8% hydrochloric acid are deep crimson, and on cooling, the separation of the salt is almost complete. The *ferri-*

chloride crystallised from acetic acid in reddish-brown, elongated, rhombic plates, exhibiting a bluish-green reflex; m. p. 200—203° (Found: C, 44·6; H, 3·9. $C_{20}H_{23}O_5Cl_4Fe$ requires C, 44·5; H, 3·9%). This derivative is readily soluble in hot acetic acid, and separates almost completely on cooling the solution.

3 : 5 : 3′ : 4′-*Tetrahydroxy*-6 : 8-*dimethylflavylium Chloride* (VI).—The chloride (1·5 g.) last described was demethylated under the usual conditions by hydriodic acid (80 c.c.; *d* 1·7) in presence of phenol (15 g.) in 30 minutes. Water (30 c.c.) was added, the phenolic layer separated, and the *iodide* precipitated by the addition of ether. The slender, red needles were collected and converted into the *chloride* by means of silver chloride in hot dilute hydrochloric acid solution. On standing, the cooled solution deposited dark red, microscopic, slender needles, and these were recrystallised from 10% hydrochloric acid (Found, in material dried in a high vacuum over sulphuric acid for 24 hours: C, 58·1; H, 5·1. $C_{17}H_{15}O_5Cl,H_2O$ requires C, 57·9; H, 4·8%). The salt is readily soluble in hot dilute hydrochloric acid, giving deep red solutions that deposit crystals but slowly on cooling. It dissolves in aqueous sodium carbonate to a bluish-violet solution, unchanged, in the absence of oxygen, by the addition of sodium hydroxide. In alcoholic solution, the sodium carbonate reaction is also violet, but this becomes blue on the addition of sodium hydroxide. The ferric chloride reaction in alcoholic solution is intense violet.

Rhamnetinidin Chloride (IX).—The crude rhamnetin obtained by hydrolysis of xanthorhamnin from Persian berries, was thoroughly extracted with boiling alcohol to remove quercetin, and then with hot acetic acid to remove rhamnazin. Finally it was purified through its monopotassium salt (Perkin and Wilson, J., 1903, **83**, 136). The light yellow product was dried at 140° (Found: MeO, 9·7. Calc.: MeO, 9·8%). A mixture of rhamnetin (4·6 g.), potassium acetate (5 g.), and acetic anhydride (80 c.c.) was boiled for 2—3 minutes (acetylation cannot be complete at this stage), and a large excess of zinc dust added in small portions in rapid succession. When further additions produced no change in the appearance of the solution (about 5 mins.), the liquid was boiled for 5 minutes longer, then cooled, decanted, and added to 500 c.c. of water containing concentrated hydrochloric acid (25 c.c.). The zinc was washed with a little acetic acid. The ochreous, sticky product was collected on a glass rod and on the sides of the container, washed with water, dissolved in alcohol (100 c.c.) and hydrochloric acid (30 c.c.), and the solution boiled for 20 minutes, the red colour of the flavylium salt appearing during this process. The crimson solution was concentrated in a vacuum, a little water being added

from time to time. When most of the colouring matter had been precipitated, the substance was collected, thoroughly extracted with a large volume of ether, and the residue with boiling 0·5% hydrochloric acid. The salt was precipitated from the filtrates, after concentration, by concentrated hydrochloric acid, and this operation was repeated. The product was then fractionally crystallised by slow evaporation of an alcoholic solution containing 10% hydrochloric acid; some tarry matter was first eliminated and then definite prismatic crystals separated. These were collected, twice recrystallised in the same way, and air-dried (Found : C, 51·9; H, 4·7; MeO, 8·3. $C_{16}H_{13}O_6Cl,2H_2O$ requires 51·6; H, 4·6; MeO, 8·6%). After this had been exposed to a vacuum for 12 hours, the analytical results indicated a monohydrate, but were not sufficiently sharp. *Rhamnetinidin chloride* is very sparingly soluble in cold 0·5% hydrochloric acid, readily soluble in the hot solvent to a brownish-red solution; the alcoholic solutions are bluish-red. The salt crystallises from aqueous-alcoholic hydrochloric acid in clusters of elongated prisms, orange-red by transmitted light, and forming a dark purplish-brown mass exhibiting an intense green reflex. On the addition of aqueous sodium carbonate to the solid salt, a blue solution is obtained. This is bluer than that of mecocyanin and redder than that of cyanidin, cyanin, or fisetinidin under the same conditions. Thick layers are violet-red, and this dichroism is the chief distinction from fisetinidin. On progressive dilution the colour becomes violet and finally blue. In alcoholic solution, the distinction from mecocyanin is much more pronounced, since with sodium carbonate under similar conditions, rhamnetinidin gives a blue solution (on the red side by comparison with cyanidin), whereas mecocyanin gives a violet solution. On the addition of sodium hydroxide to the alcoholic solution, mecocyanin and rhamnetinidin give identical pure blue colorations. The ferric chloride reaction of rhamnetinidin is blue in alcoholic solution and violet in aqueous solution.

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THE UNIVERSITY, MANCHESTER. [*Received, July 11th*, 1927.]

CCXCIV.—*A New Method of (Absolute) Potentiometric Titration.*

By BERNARD CAVANAGH.

THE following is an account of a new method of titration which combines great simplicity with the highest precision and with other special advantages. No potentiometer or standard cell is required, no normal electrode or reference "half-cell" and no mechanical stirrer, neither is any sort of liquid junction involved. Small quantities of solution can be rapidly titrated in an ordinary flask, with the aid only of a rheostat or resistance, a key, and a pointer-galvanometer. Yet the sensitivity and precision are the highest attainable by electrometric methods, and, in addition to its convenience for ordinary titrations, the method is especially suited for the titration of (*a*) very dilute solutions and (*b*) very small volumes (micro-titration).

This paper deals with the titration of the following ions: $H^{\cdot}$, $Ag^{\cdot}$, OH', Cl', Br', I'. The underlying principles will first be discussed.

1. The fundamental idea consists in the application to electrometric titration of the long-known principle of the Helmholtz cell, or cell without liquid junction. A familiar example of this type of cell is that consisting of a hydrogen electrode and either a calomel or a silver chloride electrode in one and the same solution of hydrochloric acid. The *E.M.F.* of this cell at the temperature T is given by

$$E = E_0 + 2RT/F \,.\, \log_e C\gamma,$$

where E_0 is a constant and C is the concentration of hydrochloric acid; or, if for the present we ignore the correction factor γ, *i.e.*, the "activity coefficient," and consider a particular temperature, *e.g.*, 16°, we may write

$$E = E_0 + 0{\cdot}1147 \log_{10} C \quad . \quad . \quad . \quad . \quad (1)$$

More generally, if for pure hydrochloric acid we substitute a mixed electrolyte containing hydrogen ions and chlorine ions at different concentrations, C_H and C_{Cl}, then the *E.M.F.* of the cell will be

$$E = E_0 + 0{\cdot}05735 \log (C_H \times C_{Cl}) \quad . \quad . \quad . \quad (2)$$

It is plain, therefore, that if we know E_0 and *one* of the factors C_H or C_{Cl}, we can determine the other by measuring E. This would be an example of what is commonly called a "physical" method of analysis.

Alternatively, we may gradually remove one of the ions from the solution by means of a standard reagent, the *residual* concentration

of the ion being, at each stage, indicated by the value of E, until that residual concentration either (*a*) can be neglected or (*b*) (for refined titration) reaches a certain value known to characterise the exact end-point of the titration. For instance, at the end-point in the titration of a chloride against silver, the value of C_{Cl} is equal to the solubility, S_{AgCl}, of silver chloride. The *E.M.F.* at the end-point would therefore be, in accordance with equation (2):

$$E = (E_0 + 0{\cdot}05735 \log S_{AgCl}) + 0{\cdot}05735 \log C_H \quad . \quad . \quad (3)$$

the bracketed expression being a known constant, so that the end-point *E.M.F.* depends on C_H, the acidity of the solution. A rough knowledge of C_H, however, is sufficient to permit high precision in the titration. Thus, even if C_H were estimated at *twice* its true value, the error produced in the end-point would be only $1{\cdot}5 \times 10^{-7}$ g.-equiv. per 10 c.c. of solution, which is only 1·5% in the titration of $N/1000$-solution, so that only when high precision in the most dilute solutions is required, will C_H have to be known more accurately.

Similarly, at the end-point in the titration of a strong acid by a strong base the value of C_H is equal to the acidity, h, of distilled water under the conditions prevailing. (The value of h depends ordinarily on the amount of carbon dioxide in the air and may be between 2×10^{-6} and 3×10^{-6}.) We obtain therefore a formula for the end-point potential of the same type as (3), *viz.*,

$$E = (E_0 + 0{\cdot}05735 \log h) + 0{\cdot}05735 \log C_{Cl} \quad . \quad . \quad (4)$$

so that in this case we need a rough knowledge of C_{Cl}.

It is plain that we have here a means of absolute * potentiometric titration in a single vessel without a liquid junction, and it may be observed that the resistance can thus easily be kept low, so that the method is peculiarly useful for the titration of dilute solutions without the employment of a refined galvanometer. It seems probable that the principle may be widely applicable.

2. *Elimination of the Potentiometer.*—The use of a potentiometer has been implied since we have to determine when the potential between the two electrodes reaches a certain end-point value. The instrument, it is true, need be only of simple pattern, and may be set for the end-point *E.M.F.*, so that the end of the titration is shown in practice by the reversal of the galvanometer deflexion; but we can eliminate the necessity for a potentiometer if we can

* The end-point is marked by the *E.M.F.* attaining a particular absolute value. This is the case also in the methods of Treadwell and of Müller. In all other methods, the end-point is marked by the attainment of a maximum value by the differential dE/dx, the rate of change of potential. It can be shown that the intrinsic sensitivity of the "absolute" methods is the higher.

construct a cell that will develop the required end-point *E.M.F.*, which might be done by imitating the composition which the titrated cell should have at the end-point. For instance, for the titration of a chloride, we might take a solution having the same acidity as the titrated solution, and shake it with some well-washed, precipitated silver chloride. A hydrogen electrode and a silver chloride electrode dipping into such a solution should develop the required end-point *E.M.F.* This procedure would bear the same relation to the (alternative) use of the potentiometer as the method of Treadwell bears to that of Müller.

A much simpler and more trustworthy procedure is available, however, for comparison of (1) and (3) shows that they become identical when $C^2 = S_{AgCl} \times C_H$; and it follows that if we take some hydrochloric acid of approximately the concentration C, where

$$C = \sqrt{S_{AgCl} \times C_H} = 0{\cdot}0031\sqrt{C_H} \quad . \quad . \quad . \quad (5)$$

(C_H being, as before, the acidity of the *titrated* solution), then a hydrogen and a silver chloride electrode dipped into this solution will develop the end-point *E.M.F.* This is more trustworthy than the other form of end-point cell because, the concentrations of both ions being considerable, there is less liability to polarisation during the titration. It follows from the relation (5) that, just as C_H need not be accurately known (see p. 2208), so C, the concentration of the hydrochloric acid in the end-point cell, does not require accurate adjustment.

In just the same way, for the titration of a strong acid by a strong base we obtain from (1) and (4) the relation $C^2 = hC_{Cl}$, and adopting $2{\cdot}5 \times 10^{-6}$ as a mean value for h (see p. 2208), we have

$$C = 0{\cdot}0016\sqrt{C_{Cl}} \quad . \quad . \quad . \quad . \quad . \quad (6)$$

as the strength of the hydrochloric acid solution required, in terms of the chloride concentration. (In the total absence of carbon dioxide, the numerical coefficient would be 0·0003.)

3. *The Silver Chloride–Quinhydrone Cell.*—Of late, the hydrogen electrode has been superseded for many purposes by the more convenient "quinhydrone electrode," since Biilmann showed that, for solutions not distinctly alkaline, the presence of a trace of quinhydrone in solution caused a smooth platinum electrode to behave as a reversible hydrogen electrode.

It appeared possible that an exceedingly simple form of the Helmholtz cell might be obtained by merely dipping a smooth platinum electrode and a silver chloride electrode into a solution containing hydrogen ions, chlorine ions, and a little quinhydrone, providing always that the electrodes did not interfere with one another.

In the first experiments, a plain silver wire was used, in the presence of a visible precipitate of silver chloride, but the results were unsatisfactory owing possibly to some slight catalysis of the quinhydrone reaction on the metallic surface. When, however, the silver was coated electrolytically with silver chloride, excellent and quickly reproducible results were obtained.

Many measurements were made with cells containing various proportions and concentrations of the two ions, and the results, substituted in the more exact form of equation (2), *viz.*,

$$E = E_0 + 0{\cdot}05735 \log a_H a_{Cl} \quad . \quad . \quad . \quad . \quad (7)$$

(a_H and a_{Cl} being "corrected concentrations" or activities) gave the mean value 0·4740 for E_0. The measurements covered the whole range of the titrations of both ions, up to and beyond the end-points, leaving no doubt as to the practicability of using this very simple form of cell. In fact, the results were so uniformly good as to prompt an investigation, now in progress, of the suitability of this type of cell as a means of "physical" analysis.

4. *The Silver–Quinhydrone Cell and the Solubility of Silver Chloride.*—It is of interest that, *beyond* the end-point in the chloride titration, we have in effect the rather remarkable one-solution cell, Ag | Ag^+, H^+ (quinhydrone) | Pt, or, if we regard the quinhydrone electrode as a hydrogen electrode, Ag | Ag^+, H^+ | H_2, of which the *E.M.F.* is given by

$$E = E'_0 + RT/F \,.\, \log a_{Ag}/a_H \quad . \quad . \quad . \quad . \quad (8)$$

and is thus practically unaffected by the addition of water.

The results in this region were very good and yielded the value 0·1009 for E'_0. Now the activity-product of silver chloride, and hence its true solubility in pure water, S_{AgCl}, is readily obtained from E_0 and E'_0, for

$$-\,2RT/F \,.\, \log S_{AgCl} = E_0 + E'_0 = 0{\cdot}5749 \text{ (at } 16°),$$

whence $S_{AgCl} = 0{\cdot}97 \times 10^{-5}$ at 16°, with a probable accuracy of $\pm 2\%$.

5. *Final Simplification: Elimination of the End-point Cell.*—It is evident, therefore, that the method of titration outlined in Sections 1 and 2 is fully applicable with the more convenient silver chloride–quinhydrone cell. A final simplification of apparatus and procedure, however, now becomes possible, arising out of the value of E_0, given above.* Substituting 0·4740 for E_0 and $0{\cdot}97 \times 10^{-5}$ for

* This simplification is *not* available if [the hydrogen electrode is used, because of the *negative* value of E_0 in that case.

S_{AgCl} in equation (3), we have, for the end-point potential in the titration of a chloride,

$$E_{Cl} = 0{\cdot}1866 + 0{\cdot}05735 \log C_H \quad . \quad . \quad . \quad . \quad (9)$$

this being the formula required when a potentiometer is used (see Section 12). Now calculation shows that E_{Cl} vanishes when $C_H = 5{\cdot}6 \times 10^{-4}$, *i.e.*, if the acidity of the solution is roughly $N/1800$, the end-point potential will be zero, and we require neither a potentiometer nor a second pair of electrodes to balance it. One pair of electrodes and a galvanometer is then all the physical apparatus required for the titration.

Similarly, for the acid–alkali titration, substituting for E_0 and for h in equation (4), we obtain for the end-point potential

$$E_H = 0{\cdot}153 + 0{\cdot}05735 \log C_{Cl} \quad . \quad . \quad . \quad . \quad (10)$$

which vanishes when $C_{Cl} = 2{\cdot}2 \times 10^{-3}$ (or $N/450$).

6. *The Bromide and the Iodide Cells.*—From similar series of measurements with the corresponding silver bromide (or iodide)–quinhydrone cells, the values 0·6235 and 0·8460, respectively, have been obtained for E_0, and $5{\cdot}6 \times 10^{-7}$ and $6{\cdot}5 \times 10^{-9}$ for the solubilities of the bromide and iodide. Hence we obtain for the end-point potentials:

$$E_{Br} = 0{\cdot}261 + 0{\cdot}05735 \log C_H \quad . \quad . \quad . \quad . \quad (11)$$
$$E_I = 0{\cdot}3725 + 0{\cdot}05735 \log C_H \quad . \quad . \quad . \quad (12)$$

which vanish, respectively, when $C_H = 2{\cdot}8 \times 10^{-5}$ or $3{\cdot}2 \times 10^{-7}$.

When the end-point cells are required in the titration of bromide and iodide, it is convenient still to use the hydrochloric acid cell, of which the *E.M.F.* is

$$E_{HCl} = 0{\cdot}4740 + 0{\cdot}1147 \log C \quad . \quad . \quad . \quad . \quad (13)$$

C being the concentration of the acid. Equating this in turn to E_{Br} and E_I, we obtain for the bromide $C = 0{\cdot}013\sqrt{C_H}$ (14), and for the iodide $C = 0{\cdot}12\sqrt{C_H}$ (15).

Two points must be mentioned with regard to the iodide cells, *viz.*, first, that the acidity must be kept very low—below $N/100$—because at higher concentrations the hydriodic acid reacts with the quinhydrone producing free iodine; and, secondly, that in the immediate neighbourhood of the end-point, equilibrium (and hence a reproducible potential) is only obtained after standing for ¼—½ hour with occasional shaking. Thus when high precision is required the titration of an iodide cannot be very expeditious.

7. "*Corrected Concentrations*": *Activities.*—For the sake of simplicity, the correction factors or activity coefficients, by which the concentrations are multiplied in the exact forms of the equations

given, have been ignored up to this point. It is, in fact, only when high precision is aimed at, and the most dilute solutions are titrated, that these factors need be considered: in such cases every symbol C, with or without subscript, representing a concentration (but not the symbols h, S_{AgCl}, S_{AgBr}, etc., which already represent activities), is to be multiplied by the appropriate activity coefficient, to make the formulæ exact.

Experimental.

8. *The Electrodes.*—The simpler the form of the electrodes the more easily is the surface layer of solution kept uniform with the rest by shaking.

The platinum electrodes are best free from glass so that they may the more easily be cleaned occasionally in hot sulphuric-chromic acid, and "blanked" by heating to redness for a minute or two in an alcohol flame. A form which has been found effective consists of a strip of thin foil, bent along its length to give a little rigidity, and fixed in a binding screw.

The silver halide electrodes have been made from pieces of stout silver wire about 15 cm. long by coating them, along a length of, say, 5 cm. from one end, with the appropriate halide. The wire is made the anode in the electrolysis of a dilute solution of the sodium or potassium salt, and a current of 2—3 milliamps. per sq. cm. is passed for about an hour. The wire should be turned once or twice to secure an even coating. Several electrodes can be prepared at one time, and they may be preserved in the dark for a week or more in corked tubes full of distilled water. In use, a silver halide electrode is fixed in a binding screw, and mounted in an ordinary clamp, vertically alongside and close to a platinum electrode, so that the pair will easily pass through the neck of a conical flask. We may speak of a "chloride-pair" of electrodes or a bromide- or iodide-pair, according to the nature of the silver halide electrode.

9. *The Reference Ion.*—We have seen that the potentials with which we have to deal in this method depend always on two ions, and the essential principle is that if we know the concentration of one of these ions roughly, we can titrate the other exactly. It will be convenient to speak of the ion of which the concentration must be roughly known as "the reference ion." Thus, in the titrations of the three halides the reference ion is the hydrogen ion, whilst in the titration of hydrogen ions (acids) it might be any of the three halides, but most commonly the chloride. Now in most cases, so long as the solution to be titrated is not weaker than about $N/100$ —the limit is lower in the case of bromide or iodide—*only the order of magnitude of the reference-ion concentration need be known* (see p. 2208). If, however, we are aiming at the highest precision in the

end-point, as in titrating extremely dilute solutions, we may need to know the reference-ion concentration to within a few units %, and a rough titration may be necessary to determine this.

If the reference ion is absent or nearly so, then we can easily introduce it in whatever concentration we require, by adding a little of a standard solution of sodium chloride (for Cl′) or of nitric or sulphuric acid (for H·).

It should be observed that, strictly speaking, it is the concentration at the end-point that has to be known or adjusted, and when the highest precision is required some allowance must be made for the dilution caused by the volume of reagent to be added; this can easily be done after a rough preliminary titration.

10. *The Method in its Simplest Form.*—The simplest form of procedure is applicable when the reference-ion concentration approximates to (see p. 2212), or can be adjusted roughly to, the values calculated from equations (9)—(12). All the physical apparatus required is a sturdy pointer-galvanometer (which will just detect, say, 10^{-7} amp.) in series with a rheostat, a tapping-key or plug, and one appropriate pair of electrodes, *viz.*, a chloride-pair for the titration of chloride or acid, a bromide- or an iodide-pair for the corresponding halide titrations. The deflexions of the galvanometer should be minimised by means of the rheostat so as to avoid any tendency to polarise the electrodes.

To the solution to be titrated, contained in a conical flask, a trace of quinhydrone is added (not more than 1 mg. per c.c. of solution), and most of it dissolved by gentle shaking. On raising the flask so that the pair of electrodes dips into the liquid, shaking gently, and then depressing the key, a marked deflexion of the galvanometer pointer is obtained with a high resistance in circuit, indicating a high *E.M.F.* (of the order of 0·2—0·3 volt). Some of the standard reagent is now added, and the observation of the *E.M.F.* then repeated, and so on, until eventually the *direction* of the pointer deflexion is reversed, the *E.M.F.* having reached and passed zero. This marks the end of the titration.

The indication is very sharp and sensitive. Thus the change from a deflexion representing an *E.M.F.* of 5 millivolts to the same deflexion in the reverse direction is produced, in 10 c.c. of solution, by the following quantities of reagent:

In titration of acid	3×10^{-8} g.-equiv.
„ „ „ chloride (or silver)	1×10^{-7} „
„ „ „ bromide (or silver)	6×10^{-9} „
„ „ „ iodide (slowly, see p. 2211) ...	$6{\cdot}5 \times 10^{-11}$ „

11. *The Use of the End-point Cell.*—When the concentration of the reference ion cannot conveniently be adjusted to the appropriate

value given above, it becomes necessary to add to the apparatus *either* a simple potentiometer *or* a second pair of electrodes—a chloride-pair—connected in opposition (platinum to platinum) to the first pair. In the latter case the end-point cell is completed by diluting some roughly standard hydrochloric acid approximately to the concentration C given in equation (5), (6), (14), or (15), dissolving a little quinhydrone in this solution contained in a flask or beaker, and raising the vessel on a support so that the second pair of electrodes dips into the solution. The vessel should be gently shaken occasionally during the titration.

Otherwise the titration proceeds exactly as described in Section 10, the end-point being indicated by the reversal of direction of the galvanometer deflexion, and the sensitivity being of the same order. The end-point cell can be used repeatedly for the same type of titration so long as the reference-ion concentration (C_{Cl} or C_H) in the titrated solutions remains the same.

12. *Alternative Use of a Potentiometer.*—If it is preferred to use a simple form of potentiometer to produce the end-point potential, instead of the end-point cell, it will be convenient, by means of equations (9), (10), (11), and (12), to construct tables after the following manner, giving the end-point potential for various values of the reference-ion concentration.

End-point Potential in Titration of Chloride (or Silver).

Acidity, C_H ...	1	10^{-1}	10^{-2}	10^{-3}	10^{-4}	10^{-5}
End-pt. *E.M.F.*	0·1866	0·1292	0·0719	0·0145	−0·0428	−0·1002

For intermediate values :

To {multiply / divide} C_H by.....	1·25	1·6	2	2·5	3·2
Add to / Subtract from } E the value ...	0·0055	0·0117	0·0173	0·0228	0·0290

These two tables, in conjunction with ordinary proportional interpolation, cover all probable values of C_H and E and similar tables are readily constructed for the other titrations. It would appear, however, that the second pair of electrodes, combined with a standard solution of hydrochloric acid and a measuring cylinder, constitutes a sort of " chemical potentiometer " which possesses advantages as regards bulk, cost, and immediate readiness for use over the simplest of physical instruments.

Results.

It would be superfluous to quote the results obtained in the more concentrated solutions, where the precision of the indication is greater than that of the volumetric apparatus. The results in

Table I, obtained with the more dilute solutions, indicate the limits of precision, and the order of accuracy attained requires no comment.

In order to provide a check on the *correctness* as well as the concordance of the results, the very dilute solutions were prepared by the precise dilution of carefully compared strong solutions. These gave the " calculated " results in the sixth column, from which the percentage deviations are given in the seventh column. $N/5$-Solutions of silver nitrate and the halides of potassium were compared by Volhard's method, and very good distilled water was used for the subsequent dilutions. The acid and alkali were compared at $N/2$-strength, and for the dilution of the baryta, conductivity water was used with a special arrangement to exclude atmospheric carbon dioxide.

TABLE I.

Solution titrated.	Reagent.	*R.I.A.*	*E.P.C.*	Vol. of reagent (c.c.). Found.	Calc.	Error, %.
100 C.c. of $\frac{N}{400}$-KCl	$\frac{N}{100}$-$AgNO_3$	1·0	0·0031	25·13	25·12	+0·04
		0·09	0·00093	25·135		+0·06
		0·00056	None	25·12		±0
200 C.c. of $\frac{N}{1000}$-KCl	$\frac{N}{100}$-$AgNO_3$	0·09	0·00093	20·11	20·095	+0·07
		0·01	0·00031	20·07		−0·12
		0·00056	None	20·08		−0·07
1000 C.c. of $\frac{N}{10000}$-KCl	$\frac{N}{100}$-$AgNO_3$	0·25	0·00155	10·08	10·05	+0·3
		0·04	0·00062	9·94		−1·1
		0·00056	None	9·97		−0·8
100 C.c. of $\frac{N}{5000}$-KBr	$\frac{N}{1000}$-$AgNO_3$	1·0	0·013	20·535	20·55	−0·07
		0·04	0·0026	20·53		−0·1
		$2·8 \times 10^{-5}$	None	20·56		+0·05
1000 C.c. of $\frac{N}{100000}$-KBr	$\frac{N}{1000}$-$AgNO_3$	0·09	0·0039	10·15	10·275	−1·25
		0·01	0·0013	10·22		−0·55
100 C.c. of $\frac{N}{5000}$-KI	$\frac{N}{1000}$-$AgNO_3$	0·01	0·012	20·04	20·01	+0·15
		0·0025	0·006	20·02		+0·05
1000 C.c. of $\frac{N}{100000}$-KI	$\frac{N}{1000}$-$AgNO_3$	0·0009	0·0036	9·95	10·005	−0·55
		$3·2 \times 10^{-7}$	None	10·10		+0·1
100 C.c. of $\frac{N}{400}$-HNO_3	$\frac{N}{100}$-$Ba(OH)_2$	1·0	0·0015	25·92	25·90	+0·08
		0·04	0·0003	25·89		−0·04
		0·0022	None	25·905		+0·02
200 C.c. of $\frac{N}{1000}$-HNO_3	$\frac{N}{100}$-$Ba(OH)_2$	0·25	0·00075	20·70	20·72	−0·1
		0·09	0·00045	20·71		−0·05
		0·0022	None	20·745		+0·12
1000 C.c. of $\frac{N}{10000}$-HNO_3	$\frac{N}{100}$-$Ba(OH)_2$	0·36	0·0009	10·50	10·36	+1·4
		0·09	0·00045	10·37		+0·1
		0·0022	None	10·45		+0·9

In the titrations a cheap pointer galvanometer was used throughout. The resistance of the titrated solutions was diminished by the addition of small quantities of a 10% potassium nitrate solution, prepared from Kahlbaum's "for analysis" product, twice recrystallised.

The activity coefficients depended largely on the added potassium nitrate. They were derived mainly by the use of Lewis and Randall's data ("Thermodynamics," McGraw Hill, New York, p. 382). In the third column are given the "corrected concentrations" or *activities* of the reference ion (*R.I.A.*) which were adjusted to some representative rounded values, while in the fourth column are given the activities of the hydrochloric acid in the end-point cells (*E.P.C.*), except where none was required.

Finally, it may be observed that the possibility of using a pair of very simple electrodes fixed close together and a single simple vessel for titration is not only a convenience, but also a simplification which permits the application of this method in several special ways (*e.g.*, microtitration), whilst the closeness of the electrodes and absence of liquid junction make it comparatively easy to keep the electrical resistance within bounds even at the lowest concentrations. Moreover, the elimination of the uncertainty attaching to liquid-junction potentials must facilitate greater precision.

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CCXCV.—*Nitrosation of Phenols. Part IV.* 3:5-*Dichlorophenol.*

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THE object of this investigation was to extend the work of Hodgson and Moore (J., 1923, **123**, 2499) on the nitrosation of 3-chlorophenol to the case of 3 : 5-dichlorophenol.

Blanksma (*Rec. trav. chim.*, 1908, **27**, 25) claimed to have obtained 3 : 5-dichloro-4-nitrosophenol as a by-product in the conversion of 3 : 5-dichloroaniline to the phenol, and Willstätter and Schudel (*Ber.*, 1918, **51**, 782) stated that it was obtained by the addition of sulphuric acid to an aqueous solution of the sodium salt of 3 : 5-dichlorophenol and sodium nitrite. These products, however, gave

no Liebermann nitrosoamine reaction and proved to be identical with 3 : 5-*dichloro*-4-*nitrophenol*, prepared by direct nitration of 3 : 5-dichlorophenol. Willstätter and Schudel gave no analysis for chlorine, but recorded N, 6·95%, whereas the nitro- and nitroso-compounds require N, 6·7 and 7·3%, respectively.

After numerous unsuccessful attempts, both direct and indirect, to nitrosate 3 : 5-dichlorophenol, the required substance was obtained by the oxidation of 3 : 5-*dichloro*-4-*aminoanisole* with Caro's acid and subsequent hydrolysis of the 3 : 5-*dichloro*-4-*nitrosoanisole* by concentrated sulphuric acid.

3 : 5-Dichloro-4-nitrosoanisole is colourless, and, since 4-nitrosoanisole was described by Baeyer and Knorr (*Ber.*, 1902, **35**, 3035) as bluish-green, whilst 3-chloro-4-nitrosoanisole is now shown to be deep green, the suppression of colour may be ascribed to the chlorine atom in the 5-position.

A similar explanation would apply to the colourless 3 : 5-*dichloro*-4-*nitrosophenol*, which resembles the almost colourless 3-chlorobenzoquinone-4-oxime (Hodgson and Moore, *loc. cit.*), and may better be formulated as 3 : 5-dichlorobenzoquinone-4-oxime. Kehrmann's 2 : 6-dichlorobenzoquinone-4-oxime (*Ber.*, 1888, **21**, 3318) is light yellow and decomposes at 140°, whereas its colourless 3 : 5-isomeride decomposes at 165°.

Since 3-iodophenol on nitrosation behaves differently from 3-chloro- and 3-bromo-phenols (Hodgson and Moore, 1925, **127**, 2260), the direct nitrosation of 3-chloro-5-iodophenol was attempted, but without success.

During the attempts at nitrosation, it was found that nitrous acid nitrated 3 : 5-dichlorodimethylaniline in formic acid solution (the usual procedure was fruitless); the 3 : 5-dichloro-grouping has, therefore, the same effect as in 3 : 5-dichlorophenol, which is also nitrated by nitrous acid.

EXPERIMENTAL.

The initial material, 3 : 5-dichlorophenol, was prepared from trinitrobenzene (Hodgson and Wignall, J., 1926, 2077) and also by the following modification of Willstätter and Schudel's method (*loc. cit.*): 3 : 5-Dichloroaniline (26 g.) was dissolved in 220 c.c. of hot dilute sulphuric acid (2 : 9 by vol.), the mixture cooled, and diazotised at room temperature. Excess of nitrous acid was removed by carbamide (otherwise 3 : 5-dichloro-4-nitrophenol may be formed), and the mixture added gradually to a boiling solution of sulphuric acid (100 g.) in water (140 c.c.) through which steam was passing. The aqueous distillate was made alkaline, evaporated to very small bulk, cooled, and the 3 : 5-dichlorophenol (19·5 g.)

precipitated by careful addition of 30% sulphuric acid with vigorous stirring.

3 : 5-Dichlorophenol (16 g.) was nitrated in a solution of sodium nitrate (12 g.) in water (180 c.c.) at 90—100° by the gradual addition of 48 c.c. of dilute sulphuric acid (1 : 5) during 1 hour; the mixture was then heated on the water-bath for 2 hours and steam-distilled, 3 : 5-*dichloro*-2-*nitrophenol* (5 g.) passing over, and 3 : 5-*dichloro*-4-*nitrophenol* (6 g.) being obtained from the tarry residue by repeated extraction with hot dilute hydrochloric acid.

3 : 5-Dichloro-2-nitrophenol is moderately soluble in water and readily soluble in the usual organic solvents except light petroleum, from which it crystallises in lemon-yellow needles, m. p. 51° (Found: N, 6·5; Cl, 34·0. $C_6H_3O_3NCl_2$ requires N, 6·7; Cl, 34·1%); it does not form a hydrate (compare 3-chloro-2-nitrophenol, Hodgson and Moore, J., 1926, 155), and remains unchanged when kept for 2 hours at 110°. A solid acetate could not be obtained.

3 : 5-Dichloro-4-nitrophenol is readily soluble in the usual organic solvents except light petroleum, and crystallises from water in very pale yellow needles, m. p. 150° (Found: N, 6·7; Cl, 34·1%). The *acetate*, formed when a solution of the phenol in glacial acetic acid is warmed with acetyl chloride, crystallises from dilute alcohol in colourless needles, m. p. 99° (Found: Cl, 28·2. $C_8H_5O_4NCl_2$ requires Cl, 28·4%).

Action of Nitrous Acid on 3 : 5-*Dichlorophenol*.—This was carried out according to the directions both of Blanksma (*loc. cit.*) and of Willstätter and Schudel (*loc. cit.*). In each case a product of m. p. 150° [Found: N, (i) 6·8, (ii) 6·7; Cl, (i) 34·1, (ii) 34·2. Calc. for $C_6H_3O_3NCl_2$: N, 6·7; Cl, 34·3; calc. for $C_6H_3O_2NCl_2$: N, 7·3; Cl, 37·0%] was obtained, which was identical (mixed m. p. determination) with the 3 : 5-dichloro-4-nitrophenol above; the corresponding acetates were similarly shown to be identical.

Reduction of the 3 : 5-*Dichloro*-2- *and* -4-*nitrophenols*.—3 : 5-Dichloro-2- and -4-nitrophenols are reduced to the corresponding amino-phenols by dissolving them in 12 times their weight of water containing the theoretical amount of sodium carbonate and warming the solution on the water-bath with solid sodium hyposulphite until colourless. 3 : 5-*Dichloro*-2-*aminophenol* separates from the hot solution, but in the case of the 4-*amino*-isomeride the solution has to be cooled. 3 : 5-Dichloro-2-aminophenol is readily soluble in the usual organic solvents, except light petroleum, and crystallises from water in colourless needles, m. p. 132° (Found: Cl, 39·7. $C_6H_5ONCl_2$ requires Cl, 39·9%), which darken somewhat on keeping. Its aqueous solutions give a reddish-brown precipitate with ferric chloride. 3 : 5-Dichloro-4-aminophenol is less soluble in chloroform,

carbon tetrachloride, and carbon disulphide than its 2-amino-isomeride, but more soluble in water, from which it crystallises in colourless needles, m. p. 154° (Found : Cl, 39·8%). Its aqueous solutions give a violet coloration with ferric chloride.

3 : 5-*Dichloro*-2- and -4-*nitroanisoles* are prepared by boiling for 6 hours a mixture of the appropriate nitrophenol (6 g.) with xylene (60 c.c.) and potassium carbonate (12 g.) to which methyl sulphate (12 c.c.) is gradually added. After removal of the xylene, the anisoles can be obtained pure by steam-distillation. Yield, 70% in each case. 3 : 5-Dichloro-2-nitroanisole is much more volatile in steam than its 4-nitro-isomeride, and crystallises from methyl alcohol in colourless needles, m. p. 75° (Found : Cl, 31·7. $C_7H_5O_3NCl_2$ requires Cl, 32·0%). 3 : 5-Dichloro-4-nitroanisole crystallises from methyl alcohol in colourless needles, m. p. 70° (Found : Cl, 31·9%).

3 : 5-*Dichloro*-4-*aminoanisole* is prepared by reduction of the nitro-anisole (4·2 g.) with tin (3·5 g.) and concentrated hydrochloric acid (40 c.c.), and is finally removed by steam-distillation, being much more volatile than the parent nitro-anisole. It is very soluble in methyl alcohol and carbon tetrachloride, moderately soluble in light petroleum, and only slightly soluble in water or dilute acids; it crystallises from dilute methyl alcohol in colourless needles, m. p. 71° (Found : Cl, 36·7. $C_7H_7ONCl_2$ requires Cl, 37·0%).

3 : 5-*Dichloro*-4-*nitrosoanisole* was obtained by oxidation of the amino-anisole with Caro's acid as follows : Potassium persulphate (16 g.) was stirred into concentrated sulphuric acid (32 g.), kept at room temperature for 1 hour, then poured on ice and neutralised with potassium carbonate, the final volume being about 250 c.c. The mixture was rendered faintly acidic with acetic acid, added with stirring to a cold suspension of finely-divided 3 : 5-dichloro-4-amino-anisole (2·5 g.) in 200 c.c. of water, and kept for 24 hours, the stirring being maintained for the first 6 hours; the solid product was filtered off, and unchanged amine removed from it by extraction with warm very dilute hydrochloric acid. The crude product (1·5 g.; m. p. 122°) was crystallised from carbon tetrachloride and then from methyl alcohol; colourless needles, m. p. 125° (Found : Cl, 34·23. $C_7H_5O_2NCl_2$ requires Cl, 34·46%). The nitroso-anisole turns green on melting but becomes colourless again on solidifying, and is readily soluble in chloroform and acetone, but more sparingly soluble in carbon tetrachloride, benzene, and methyl alcohol, forming green solutions; it is insoluble in light petroleum and gives the Liebermann nitrosoamine reaction.

3 : 5-*Dichloro*-4-*nitrosophenol* [-*quinone*-4-*oxime*(?)] is obtained by heating 3 : 5-dichloro-4-nitrosoanisole (1 g.) with concentrated

sulphuric acid (10 c.c.) on the water-bath for ½ hour—longer periods produce charring. An odour of quinone is noticeable during the hydrolysis. On pouring the mixture on ice, a colourless solid separates, which completely dissolves in alkalis to a green solution. The product gives the Liebermann nitrosoamine reaction, is soluble in methyl alcohol, ether, acetone, and glacial acetic acid, sparingly soluble in water, benzene, nitrobenzene, and chloroform, and insoluble in light petroleum and carbon disulphide. It separates from dilute acetic acid in colourless leaflets, which turn light brown on exposure and decompose at 165° (Found: N, 7·4; Cl, 36·9. $C_6H_3O_2NCl_2$ requires N, 7·3; Cl, 37·0%). No change appears to be effected by alkalis but decomposition takes place with boiling acids.

Among the unsuccessful attempts to prepare the foregoing nitrosophenol may be mentioned the use of: (1) Aqueous solutions of the sodium salt of 3 : 5-dichlorophenol and sodium nitrite, which gave only the 4-nitrophenol on acidification under a variety of conditions; (2) formic and acetic acid solutions; (3) amyl nitrite (compare Henrich and Rodins, *Ber.*, 1902, **35**, 4192); (4) nitrosylsulphuric acid; (5) nitrous gases and an ethereal solution of 3 : 5-dichlorophenol. The materials used as the starting-point of indirect methods included (1) 3 : 5-dichlorodimethylaniline; (2) 3 : 5-dichloro-4-aminophenol (oxidation by Caro's acid; also diazotisation, followed by oxidation with ferricyanide).

An Example of Simultaneous Reduction and Chlorination.—Reduction of 3-chloro-4-nitroanisole (6 g.) with tin (6 g.) and concentrated hydrochloric acid (50 c.c.) gave 2·5 g. of 3 : 5-dichloro-4-aminoanisole. Iron and acetic acid, or tin and dilute hydrochloric acid, however, effected normal reduction to 3-chloro-4-aminoanisole (compare Hodgson and Handley, J., 1926, 542).

3-*Chloro*-4-*nitrosoanisole* is obtained when 3-chloro-4-aminoanisole hydrochloride (3·5 g.), dissolved in water (300 c.c.), is treated with sodium hydroxide (0·7 g.) then rendered faintly acidic with acetic acid, and oxidised by potassium persulphate (20 g.) as above. The product is almost insoluble in light petroleum, but readily dissolves in the usual organic solvents, forming green solutions; from methyl alcohol it crystallises in deep green needles, m. p. 59° (Found: Cl, 20·4. $C_7H_6O_2NCl$ requires Cl, 20·7%), which give the Liebermann nitrosoamine reaction.

Action of Nitrous Acid on 3 : 5-*Dichlorodimethylaniline.*—3 : 5-Dichlorodimethylaniline was best prepared by heating 3 : 5-dichloroaniline (8 g.), methyl sulphate (12 c.c.), and methyl alcohol (15 c.c.) for 5 hours in a sealed tube at 165—170° (great pressure is developed). The viscous red product was poured into water (100 c.c.) and kept

for 1 hour until solid. Yield 4 g. It crystallises from dilute methyl alcohol (charcoal) in colourless, rhombic plates, m. p. 55° (Found : Cl, 37·3. Calc. : Cl, 37·4%), which are readily soluble in the usual organic solvents.

Attempts to nitrosate this compound by the usual methods having proved fruitless, the following method was attempted : 3 : 5-Dichlorodimethylaniline (3·8 g.), dissolved in formic acid (15 c.c.), was treated at 0° with finely powdered sodium nitrite (1·4 g.). The brown needles which first formed rapidly became resinous, and, after separation, the product was extracted with a mixture of equal parts of alcohol and acetic acid and then recrystallised from methyl alcohol; golden needles, m. p. 142° (Found : Cl, 30·1.

$$C_6H_2NMe_2Cl_2\cdot NO_2$$

requires Cl, 30·2; $C_6H_2NMe_2Cl_2\cdot NO$ requires Cl, 32·4%). This product is readily soluble in acetic acid but sparingly soluble in methyl alcohol.

Nitration of 3 : 5-*Dichlorodimethylaniline*.—To 3 g. of the dichlorodimethylaniline in concentrated sulphuric acid (12 c.c.) at 0°, nitric acid (1 c.c.; 91%) was gradually added during 1 hour. The mixture was kept for a further hour at 0°, then poured on ice, and the resulting solid was filtered off, washed with cold alcohol, and crystallised from methyl alcohol; golden needles, m. p. 142° (Found : Cl, 30·3%). This product, 3 : 5-*dichloro*-4-*nitrodimethylaniline*, was identical with the preceding substance (mixed m. p. determination), thereby establishing the fact that 3 : 5-dichlorodimethylaniline is nitrated by nitrous acid in formic acid solution.

3 : 5-Dichloro-4-nitro-dimethylaniline is not decomposed on boiling with aqueous alkaline hydroxides.

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TECHNICAL COLLEGE, HUDDERSFIELD. [*Received, August 5th*, 1927.]

CCXCVI.—*The Abnormal Reaction of Certain Aromatic Aldehydes with Schiff's Reagent.*

By JOHN BALDWIN SHOESMITH, CHARLES EDWIN SOSSON, and ARTHUR CLEMENT HETHERINGTON.

WIELAND and SCHEUING (*Ber.*, 1921, **54**, 2527) have recently carried out an investigation on the nature of Schiff's reagent and the colour obtained in its reaction with aldehydes, and conclude that

the essental constituent of the reagent is an *N*-sulphinic acid of pararosaniline-*C*-leucosulphonic acid,

$$SO_3H\cdot C(C_6H_4\cdot NH_2)_2\cdot C_6H_4\cdot NH\cdot SO_2H.$$

To the soluble violet dyestuff produced on the admixture of the reagent with acetaldehyde they ascribe the formula

$$NH{:}C_6H_4{:}C[C_6H_4\cdot NH\cdot SO\cdot O\cdot CH(OH)\cdot CH_3]_2.$$

There are several references to abnormalities in the Schiff aldehyde reaction in the literature (compare Lorenz, *Ber.*, 1881, **14**, 789; Schmidt, *ibid.*, p. 1840; Bela von Bitto, *Z. anal. Chem.*, 1897, **36**, 369; Paula and von Buttlar, *Annalen*, 1911, **383**, 230), and one of us has remarked on the behaviour of salicylaldehyde (J., 1923, **123**, 2700) and β-resorcylaldehyde (*ibid.*, p. 2705) in giving yellow colorations and precipitates, in place of the usual soluble dyestuff, under certain conditions.

Investigations have been carried out with a view to discovering (1) the class of aldehyde which gives these abnormal yellow precipitates with Schiff's reagent; (2) the conditions under which these precipitates are formed—because it was afterwards discovered that red colorations and precipitates are produced under other conditions; and (3) the nature of this abnormal reaction and the composition of the precipitates.

Of the large number of aldehydes examined ortho-hydroxy-aromatic aldehydes most readily give yellow precipitates; indole-aldehyde behaves similarly. The reaction product is chiefly dependent on the quantity of sulphur dioxide capable of neutralising iodine (afterwards referred to as "free" sulphur dioxide) present in the reagent, as is seen from the Table, in which Y = yellow, O = orange, R = red, P = purple, B = brown, subscript p = precipitate, subscript c = coloration, and g. = g. of "free" sulphur dioxide per 100 c.c. of reagent.

	g. = 19	10	1·0	0·25	0·1
Aldehyde.			Reaction.		
Salicylaldehyde	P_c	P_p	Y_p	Y_p	Y_p
p-Hydroxybenzaldehyde	P_c	P_c	P_p	Y_p	Y_c
β-Resorcylaldehyde	P_p	Y_p	Y_p	Y_p	Y_p
Dihydroxy*iso*phthalaldehyde	R_p	Y_p	Y_p	Y_p	Y_p
2 : 3 : 4-Trihydroxybenzaldehyde	Y_c	Y_c	Y_c	Y_c	Y_c
p-Methoxysalicylaldehyde	R_p	R_c+Y_p	Y_p	Y_p	Y_p
Vanillin	P_p	B_p	Y_p	Y_p	Y_p
Orcylaldehyde	R_p	Y_p	Y_p	Y_p	Y_p
α-Orcindialdehyde	R_p	Y_p	Y_p	Y_p	Y_p
Indole-3-aldehyde	R_p	Y_p	Y_p	Y_p	Y_p
2-Hydroxy-3-methylbenzaldehyde	R_p	Y_p	Y_p	Y_p	Y_p
2-Hydroxy-4-methylbenzaldehyde	R_p	Y_p	Y_p	Y_p	Y_p
2-Hydroxy-5-methylbenzaldehyde	R_p	Y_p	Y_p	Y_p	Y_p
2-Hydroxy-1-naphthaldehyde	O_p	O_p	O_p	O_p	O_p
1-Hydroxy-2-naphthaldehyde	R_c+O_p	O_p	O_p	O_p	O_p
Cinnamaldehyde	P_p	P_p	P_p	B_p	B_p

The following aldehydes, chosen as representatives of other classes, behave normally, in that red or purple solutions are obtained under all the above conditions: Benzaldehyde, *m*-hydroxy-, and *o*-, *m*-, and *p*-methoxy-benzaldehydes; *o*-, *m*-, and *p*-nitro-, *o*-chloro-, *o*- and *m*-fluoro-, *m*- and *p*-bromo-, *p*-methyl-, 2-nitro-4-methoxy-,* 3-nitro-4-methoxy-benzaldehydes; 3 : 4-methylenedioxybenzaldehyde ($P_p + V_o$); *iso*propyl- and 2-carboxy-3 : 4-methylenedioxybenzaldehydes; α-naphthaldehyde, and its 3-* and 5-methoxy- and 5-bromo-derivatives; 5-bromo-2-naphthaldehyde; acrolein (deep blue), *iso*butyric aldehyde, glycollaldehyde, and glyoxal. It is noteworthy that 2 : 4-dimethoxybenzaldehyde, 2-methoxy-1-naphthaldehyde,† and thioacetaldehyde were neutral towards the reagent, and that resacetophenone and 2 : 4 : 2′ : 4′-tetrahydroxybenzophenone gave a violet coloration very slowly—in sharp contrast to β-resorcylaldehyde, which reacts rapidly.

In general, *o*-hydroxy-aromatic aldehydes give the yellow precipitates most readily, but exceptions to the rule are afforded by *p*-hydroxybenzaldehyde, which gives the yellow reaction when only a trace of " free " sulphur dioxide is present, by vanillin, by cinnamaldehyde and indole-aldehyde.

In order to ascertain the composition of the precipitates, that obtained from β-resorcylaldehyde was examined in detail. They cannot be separated as pure compounds owing to their insolubility in organic solvents or water, and to their instability towards acids and alkali. Analytical results were therefore only approximate, but a satisfactory clue to the constitution of the precipitate in each case was obtained from the interaction of the aldehyde with reagents in which the base employed was analogous to pararosaniline.

Neither the yellow nor the red *precipitates* have a constitution approximating to that proposed by Wieland and Scheuing for the dyestuff. The two classes of precipitates have very nearly, but not quite, the same constitution. When they are first formed their behaviour corresponds with that which would be expected of sulphites of hydrated Schiff's bases formed from the aldehyde and pararosaniline-*C*-leucosulphonic acid, $SO_3H{\cdot}C(C_6H_4{\cdot}NH_2)_3$—the basic constituent of Schiff's reagent. These sulphites, on drying over calcium chloride or potassium hydroxide, slowly lose sulphur dioxide; and after complete removal of the " sulphite " sulphur dioxide by dilute aqueous sodium bicarbonate, the final dried

* These aldehydes have not been described in the literature and were prepared in connexion with other investigations, an account of which, it is hoped, will be published shortly.

† This is probably due to steric hindrance, because in another investigation it was found impossible to convert the aldehyde to the alcohol by the well-known methods which readily served in other cases.

substance has properties that would be associated with, and a composition approximating to that of, a hydrated Schiff's base of formula $SO_3H{\cdot}C[C_6H_4{\cdot}NH{\cdot}CH(OH){\cdot}C_6H_3(OH)_2]_3$. On careful hydrolysis with 10% aqueous sodium hydroxide, in which the precipitates are soluble, it was possible to recover the aldehyde in a quantity corresponding to that expected from the above formula, but the recovered pararosaniline could not be estimated. Hence we regard the reaction with this type of aldehyde as being $SO_3H{\cdot}C(C_6H_4{\cdot}NH_2)_3 + 3R{\cdot}CHO + xH_2SO_3 \longrightarrow SO_3H{\cdot}C[C_6H_4{\cdot}NH{\cdot}CH(OH)R]_3(H_2SO_3)_x$, the sulphurous acid acting as a catalyst in the formation of the "Schiff's base."

This suggestion is substantiated by the production of the yellow precipitates from pure pararosaniline-*C*-leucosulphonic acid and β-resorcylaldehyde in sulphurous acid solution, and also of precipitates, which are analogous in appearance, constitution, and general properties, from the aldehyde and the following: (*a*) the leucosulphonic acid in hydrochloric acid solution, this acid taking the place of sulphurous acid as a catalyst, and the resulting precipitate being a hydrochloride, and not a sulphite; (*b*) sulphurous acid solutions of *p'p''p'''*-triaminotriphenylmethane; (*c*) *p'p''*-diaminotriphenylcarbinol; (*d*) *p'p''*-diaminotriphenylmethane; or (*e*) *p*-aminotriphenylmethane. It was not possible to obtain the simplest analogue of Schiff's reagent, *i.e.*, a sulphurous acid solution of *p*-aminotriphenylcarbinol.

The reaction of Schiff's reagent in the normal case is considered by Wieland and Scheuing to involve the production of a compound in which carbon and nitrogen are indirectly united through sulphur dioxide, *i.e.*, the formation of an aldehyde-bisulphite type, whilst in the abnormal cases the C–N union is direct, *i.e.*, of the Schiff's base or anil type. The presence of large quantities of sulphur dioxide in the reagent favours the bisulphite reaction and also retards the Schiff's base reaction, and thus in some of the cases examined, *e.g.*, salicylaldehyde, a small quantity of the red dyestuff is produced with Schiff's reagent saturated with sulphur dioxide. The red precipitates are therefore really yellow ones which have adsorbed a little of the red dyestuff, but not sufficient to make the analytical results for the two classes markedly different.

It is not yet understood why the aldehydes given above should behave in this abnormal manner towards Schiff's reagent.

EXPERIMENTAL.

Reaction of β-Resorcylaldehyde towards Schiff's Reagent.

The reagent was prepared by allowing 10 g. of pure pararosaniline (Kahlbaum) to stand at the ordinary temperature in 500 c.c. of

saturated aqueous sulphur dioxide; when the solution became colourless 200 c.c. were added to a (saturated) solution of 8 g. of β-resorcylaldehyde in 1000 c.c. of water at 20°. The freshly prepared reagent produced a red coloration followed by a red precipitate; a yellow precipitate then formed slowly under ordinary conditions, but very rapidly if sulphur dioxide was removed from the solution under diminished pressure. From a separate portion of the reagent, the sulphur dioxide was removed, and samples were used at various concentrations of "free" sulphur dioxide (1) to estimate the amount of sulphur dioxide present, by titration with iodine, and (2) to investigate the effect of loss of sulphur dioxide from the reagent on the nature of the reaction. The results are summarised on p. 2222.

The solids were filtered and they then dissolved in aqueous alkali—the yellow with an orange colour, the red with a purple colour—and from these solutions the original solid could be immediately reprecipitated by the addition of acid. If allowed to stand in such a solution, the solids were hydrolysed (very rapidly if the solutions were heated) and a purple solid, pararosaniline, was precipitated along with a little tar. After this was filtered off, acidification of the alkaline solution produced a strong odour of sulphur dioxide, and β-resorcylaldehyde could be extracted from the acid liquid with ether, thus showing the essential constitution of the solids to be: aldehyde, pararosaniline, and sulphur dioxide.

For analysis, the solids were filtered and dried in a desiccator. The red remained unchanged in colour, but the yellow slowly lost sulphur dioxide and water, becoming dark green, and only became yellow again on the addition of *sulphurous acid*, and not on the addition of either water or sulphur dioxide alone. The loss of sulphur dioxide and the concomitant colour change were continuous as shown by sulphur estimations (see below) at intervals. The last trace of sulphur remaining in the solids as sulphite (but not that on the central carbon atoms of the rosaniline) was removed by dilute aqueous sodium bicarbonate, which caused the sample which was originally yellow to become deep green, but did not affect the colour of the red sample.

Sulphur estimations (*Carius*). Yellow solid: 2 days, 7·16; 1 week, 5·6; 2 months, 4·0; after washing with $NaHCO_3$, 2·8%. (Last sample had N, 4·4%.) Red solid: 1 week, 6·0; 2 months, 4·3; after washing with $NaHCO_3$, 3·2%. (Last sample had N, 5·1%.) The last sample from the yellow compound, which had been thoroughly dried over calcium chloride, was further dried over concentrated sulphuric acid in a vacuum. The last treatment caused a loss of 7·2%, which is ascribed to loss of water from any

–NH·CH(OH)– groups present (compare Dimroth and Zoeppritz, *Ber.*, 1902, **35**, 996).

In order to demonstrate the catalytic action of the sulphurous acid, pararosaniline-*C*-leucosulphonic acid (Wieland and Scheuing, *loc. cit.*) was dissolved in (*a*) sulphurous acid and (*b*) dilute hydrochloric acid, and on the addition of an aqueous solution of β-resorcylaldehyde to these solutions, a yellow precipitate {Found: N, 4·4; S, 2·9. $SO_3H·C[C_6H_4·NH·CH(OH)·C_6H_3(OH)_2]_3$ requires N, 5·4; S, 4·1%} was produced in the former case, identical in all respects with that from the aldehyde and Schiff's reagent, and a greenish-yellow precipitate {Found: N, 4·4; Cl, 8·5; S, 2·75. $SO_3H·C[C_6H_4·NH·CH(OH)·C_6H_3(OH)_2,HCl]_3$ requires N, 4·7; Cl, 11·8; S, 3·5%} in the latter case; this differed from the yellow precipitate in containing hydrolysable chlorine, *i.e.*, it was the hydrochloride instead of the sulphite. Since it was impossible to recrystallise either of the solids, the analytical results only approximate to those of pure compounds, and it appears as if some of the nitrogen atoms combined with two aldehyde residues, causing the low results for S, N, and Cl.

The quantity of aldehyde present in the precipitate was determined as follows, the method being trustworthy to within ± 2%: A weighed quantity of the solid was hydrolysed with boiling 8% aqueous sodium hydroxide, the solution cooled, filtered from pararosaniline, almost neutralised with dilute hydrochloric acid, and made up to 50 c.c. Phenolphthalein was added, followed by hydrochloric acid drop by drop until the solution was just colourless; methyl-orange was then added and the solution titrated with standard acid. This was a measure of the aldehyde in the original compound, since β-resorcylaldehyde is acid to phenolphthalein,* but does not affect methyl-orange. An addition of 0·1 c.c. of the acid was required to correct for the change from p_H 7—9 (sensitivity to phenolphthalein) to p_H 3—5 (sensitivity to methyl-orange). The yellow solid contained 56% of aldehyde, and the red 50%; $SO_3H·C[C_6H_4·NH·CH(OH)·C_6H_3(OH)_2]_3$ requires 52%. The aldehyde content should be higher than that given by the titration method but the tar probably contained a little aldehyde which resisted aqueous extraction.

Influence of Sulphurous and Hydrochloric Acids on the Rate of Precipitation of Schiff's Base.—A standard solution of each acid

* Although β-resorcylaldehyde behaves as a monobasic acid towards alkali in presence of phenolphthalein (compare *Annalen*, 1911, **383**, 288), 4 : 6-dihydroxy*iso*phthalaldehyde behaves partly as a mono- and partly as a di-basic acid, and cannot be estimated in the same manner.

was in turn added to a dilute aqueous solution of aniline (3%), which was then immediately added to a 5% solution of β-resorcylaldehyde, the tube shaken, and the time (t) noted for the appearance of the precipitate. In each case, increasing concentration of acid first diminished and then increased the time required:

G. of SO_2 per 100 c.c. of solution.	t (secs.).	G. of HCl per 100 c.c. of solution.	t (secs.).
0·0	115	0·0	110
0·026	75	0·0073	100
0·066	60	0·0803	15
0·092	20	0·3285	15
0·118	20	0·4280	20
0·170	45	0·5840	95
0·298	200	0·8760	>300

Condensation of Resorcylaldehyde with Bases analogous to Triphenylmethane-C-leucosulphonic Acid.

Preparation of Bases.—p'p''p'''-*Triaminotriphenylmethane.* Finely powdered, dried triphenylmethane (10 g.) was slowly added to a constantly stirred mixture of 78 g. of nitric acid (d 1·42) and 120 g. of concentrated sulphuric acid at — 5—0°, and after the temperature of the whole had been allowed to rise slowly to about 15° (½ hour), the reaction mixture was poured into much cold water, and the solid trinitrotriphenylmethane was filtered off, boiled with 75% acetic acid, filtered, dried, and recrystallised from chloroform–ether; m. p. 212·5° (yield, 65%).

The trinitro-compound was dissolved in boiling glacial acetic acid, and to the red solution zinc powder was added until the colour had disappeared. The whole was diluted with water, excess of zinc filtered off, ammonia added to the solution, and the base filtered, dried, dissolved in dilute hydrochloric acid, the hydrochloride precipitated by the addition of concentrated hydrochloric acid, and finally dissolved in water, from which the free base was precipitated with ammonia, filtered, dried, and recrystallised from absolute alcohol. It had m. p. 201°.

pp'-*Diaminotriphenylmethane.* This was prepared by a slight modification of Baeyer and Villiger's method (*Ber.*, 1904, **37**, 2860); part of it was acetylated, and the diacetyl derivative (m. p. 233—234°) was oxidised to the carbinol, which was purified by conversion to the hydrochloride (Doebner's violet) and reprecipitation with ammonia. It had m. p. 173°.

p-*Aminotriphenylmethane.* A mixture of benzhydrol (5 g.) (from benzophenone), aniline hydrochloride (3·5 g.), and powdered anhydrous zinc chloride (4 g.) was immersed for 20 hours in the vapour of a mixture of toluene and xylene at 140°—this temperature

is of extreme importance. The whole was cooled, the tube broken, washed with water, shaken with a mixture of ether and sulphuric acid, and the curdy, insoluble amine sulphate filtered off, recrystallised from water, dried, extracted with ether (Soxhlet) until no brown coloration of the ether was observed, and finally dissolved in much boiling water; the base was then precipitated by sodium hydroxide and crystallised from light petroleum (aggregates of colourless plates, m. p. 84·5°). The acetyl derivative had m. p. 167° (compare Baeyer and Villiger, *loc. cit.*).

p-*Aminotriphenylcarbinol.* The methane was oxidised as in the case of the diamino-compound (compare Baeyer and Lohr, *Ber.*, 1890, **23**, 1623). *p*-Acetamidotriphenylcarbinol crystallises in fine, lustrous needles, m. p. 175·5°. To obtain the free amine, the pure acetyl derivative (4·5 g.) was mixed with 250 c.c. of dilute sulphuric acid (1 in 5) and 30 c.c. of alcohol, and the whole was boiled until clear (3 hours). The solution was filtered and caustic soda added to the hot filtrate (not sufficient to neutralise it) until a few drops gave a crystalline deposit on cooling. The bulk of the solution was then allowed to cool, and the aminotriphenylcarbinol sulphate crystallised in orange plates, which were dried and extracted in a Soxhlet, as in the case of the diamino-compound. The pure sulphate was then dissolved in hot water and the base precipitated with ammonia. It had m. p. 115°, but could not be obtained in a crystalline condition from any solvent (compare Baeyer and Lohr, *loc. cit.*).

Unlike the di- and tri-amino-derivatives, the mono-amino-carbinol is not readily soluble in sulphurous acid, and in an attempt to prepare the *C*-leucosulphonic acid by dissolving the carbinol in hot sulphurous acid solution, a crystalline solid was obtained of m. p. 125—128° (decomp.) (Found: N, 3·72; S, 5·6). The compound most nearly corresponding to this is the sulphite

$$[(C_6H_5)_2C(OH)\cdot C_6H_4\cdot NH_2]_2,H_2SO_3,$$

which requires N, 4·4; S, 5·1%. When heated on the water-bath, the crystals became deep orange in colour, in agreement with the fact that feebly coloured salts of the carbinol become deeply coloured when heated. Hence the *C*-leucosulphonic acid could not be obtained because of the insoluble nature of the sulphite first formed on the addition of sulphurous acid to the carbinol.

Aqueous solutions of the aldehyde were mixed with sulphurous acid solutions of the above bases in order to trace the regularity in sulphur and nitrogen content of the precipitates. The estimations were carried out after the solids had been washed with aqueous sodium bicarbonate and dried, and the results are summarised as follows.

Amine.	N%.	S%.	Calc. for 1 aldehyde to each NH_2-group N%.	S%.
$CH(C_6H_4\cdot NH_2)_3$	5·3	trace	5·97	0·0
$CHPh(C_6H_4\cdot NH_2)_2$	4·6	,,	5·06	0·0
$CPh(OH)(C_6H_4\cdot NH_2)_2$	4·1	3·4	4·43	5·1
$CHPh_2\cdot C_6H_4\cdot NH_2$	3·5	0·0	3·5	0·0

It is thus seen that only in the cases of the carbinols where *C*-leucosulphonic acids are formed is any appreciable quantity of sulphur left in the solids, and the proportion of nitrogen falls quite regularly with number of amino-groups present. It is also noteworthy that all the precipitates contained sulphur until washed with dilute bicarbonate, and that the colour change was not so marked in the case of the methanes as the carbinols.

Condensations of Other Aldehydes with Schiff's Reagent.—The aldehydes used here were prepared by the methods given in the literature.* The majority of these were almost insoluble in water and hence were first dissolved in alcohol, which had to be freed from traces of aldehyde. For this purpose it was boiled with solid caustic soda and distilled, the middle fraction being mixed with about 2 c.c. of Schiff's reagent and again fractionated; the first portion was rejected, but about 1 l. of alcohol, which gave a very faint pink colour with Schiff's reagent only after the lapse of ½ hour, was thus obtained. The aldehyde to be tested (0·25 g. approx.) was then dissolved in 5 c.c. of the alcohol, 5 c.c. of the reagent (made up as before) were added, and the mixture was very gently shaken to avoid atmospheric oxidation of the alcohol. The results are given on p. 2222.

Note on the Stability of Schiff's Reagent.—As is well known, Schiff's reagent when heated develops a red colour similar to that obtained in normal aldehyde reactions. It has been found that this colour disappears when the solution is cooled if it has not been either boiled or heated for a considerable time, for the appearance and disappearance of the colour depend on the amount of sulphur dioxide present in this solution. Damianovich (*Chem. Abs.*, 1910, **4**, 1681) heated Schiff's reagent in a sealed tube, and therefore noted the same phenomenon. *pp'*-Diaminotriphenylcarbinol behaves in exactly the same way, the development of a deep violet colour in the heat and its disappearance in the cold being very striking. Absorption spectra were photographed and the bands were almost identical in the first case with those observed in pararosaniline hydrochloride, and in the second case with those in Doebner's violet. A colour change was also noted in the case of

* Neither orcinol nor indole condenses with diphenylformamidine to give an aldehyde-anil (compare Shoesmith and Haldane, J., 1923, **123**, 2705).

the mono-amino-compound and here the hot solution was yellow and the cold colourless, but for reasons given this was not so satisfactory as the others. Wieland and Scheuing (*loc. cit.*) have proved that when Schiff's reagent is boiled until a precipitate appears the following reaction takes place:

$$2C(NH_2\cdot C_6H_4)_2(SO_3H)\cdot C_6H_4\cdot NH\cdot SO_2H \longrightarrow \underset{(A.)}{} \quad C(NH_2\cdot C_6H_4)_3\cdot SO_3\cdot NH_2{:}C_6H_4{:}C(C_6H_4\cdot NH_2)_2.$$
$$\underset{(B.)}{}$$

The formation of the colour suggests that an intermediate stage has been observed and that the full cycle of changes is as follows:

$$A \underset{\text{Cooled (}SO_2\text{ regained by C)}}{\overset{\text{Heated (}SO_2\text{ lost to solution)}}{\rightleftharpoons}} (NH_2\cdot C_6H_4)_3C\cdot SO_3H \underset{\text{Cooling}}{\overset{\text{Further heating}}{\rightleftharpoons}} (NH_2\cdot C_6H_4)_2C{:}C_6H_4{:}NH,H_2SO_3$$
$$(C.) \qquad (D;\ \text{coloured})$$

$$\downarrow \text{Loss of } SO_2 \text{ from boiling solution}$$

$$(NH_2\cdot C_6H_4)_2C{:}C_6H_4{:}NH \quad (E.)$$

Unchanged C combines with E to form B by salt formation.

In order to avoid this disadvantage of Schiff's reagent, a "modified reagent" has been suggested independently by Prudhomme (*Bull. Soc. Ind. Mulhouse*, 1904, **74**, 169) and by Wertheim (*J. Amer. Chem. Soc.*, 1922, **44**, 1834), which is prepared from pararosaniline and sodium hyposulphite. Towards such a reagent the *o*-hydroxybenzaldehydes behave as towards a Schiff's reagent containing about 1 g. of "free" sulphur dioxide per 100 c.c.

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EDINBURGH UNIVERSITY. [*Received, June 27th*, 1927.]

CCXCVII.—*The Action of Phosphorus Pentabromide on the Isomeric β-Methoxyphenylethyl Alcohols.*

By JOHN BALDWIN SHOESMITH and ROBERT JORDAN CONNOR.

DURING attempts to prepare the isomeric β-methoxyphenylethyl bromides by the method which served for the corresponding methyl derivatives (Shoesmith and Connor, this vol., p. 1768), it has been discovered that when the phosphorus pentabromide reacts with the isomeric β-methoxyphenylethyl alcohols, the nuclear directing power of the methoxyl group is so great that it causes the formation of

nuclear-brominated derivatives of the expected β-methoxyphenylethyl bromides. Thus the only compounds isolated in a pure state are β-5-*bromo*-2-*methoxyphenylethyl bromide* from the ortho-alcohol, β-6-*bromo*-3-*methoxyphenylethyl bromide* from the meta-, and β-3-*bromo*-4-*methoxyphenylethyl bromide* from the para-alcohol. The orientation of the disubstituted β-phenylethyl bromides has been proved in each case by oxidation to the corresponding known bromomethoxybenzoic acid.

Whilst carrying out preliminary experiments on the most satisfactory methods for obtaining substituted β-phenylethyl alcohols, the authors found that β-phenylethylamine in aqueous hydrochloric acid yields with nitrous acid an appreciable quantity of β-phenylethyl chloride in sharp contrast to the production of pure alcohols from the isomeric tolylmethylamines (Shoesmith and Slater, J., 1924, **125**, 2278).

Experimental.

Three series of reactions by which the isomeric β-methoxyphenylethyl alcohols might conceivably be prepared were investigated :

(1) $R\cdot CHO \xrightarrow{CH_2(CO_2H)_2} CHR{:}CH\cdot CO_2H \xrightarrow[\text{amalg.}]{Na} CH_2R\cdot CH_2\cdot CO_2H \xrightarrow[+NH_3]{SOCl_2} CH_2R\cdot CH_2\cdot CONH_2 \xrightarrow{NaOCl} CH_2R\cdot CH_2\cdot NH_2 \xrightarrow{HNO_2} CH_2R\cdot CH_2\cdot OH$ (Haworth, Perkin, and Rankin, J., 1924, **125**, 169).

(2) $R\cdot CHO \xrightarrow[+\text{alkali}]{CH_3NO_2} CHR{:}CH\cdot NO_2 \xrightarrow[\text{acid}]{Zn+} CH_2R\cdot CH{:}NOH \xrightarrow[\text{amalg.}]{Na} CH_2R\cdot CH_2\cdot NH_2 \longrightarrow CH_2R\cdot CH_2\cdot OH$ (Rosenmund, *Ber.*, 1909, **42**, 4778).

(3) $R\cdot Br \xrightarrow[CH_2Cl\cdot CH_2OH]{Mg+} CH_2R\cdot CH_2\cdot OH$ (Grignard, *Compt. rend.*, 1905, **141**, 44).

The yield of amine obtained by scheme (1) was much better than that by (2), but the poor yield of alcohol from amine led to the adoption of (3), which involved the laborious preparation of large quantities of the isomeric bromoanisoles.

The following is the best method for the preparation of *o*-methoxybenzaldehyde [used in (1) and (2)] in quantity : Salicylaldehyde (122 g.) was emulsified in a flask fitted with a reflux condenser by vigorous stirring with 40 c.c. of water, and a solution of potassium hydroxide (85 g. in 160 c.c. of water) added alternately with methyl sulphate (157 g.). The appearance and disappearance of the yellow colour of the potassium compound of the aldehyde served as an excellent indication of the course of the reaction; excess of alkali was avoided and hence the reaction temperature could be allowed to

rise without affecting the yield, which was always about 100 g., b. p. 236—237°.

The amines obtained in series (1) had b.p.'s as follows: R = C_6H_5, 88—89°/18 mm.; R = *o*-MeO·C_6H_4, 127—128°/21 mm.; R = *m*-MeO·C_6H_4, 126—127°/14 mm.; R = *p*-MeO·C_6H_4, 131—132°/18 mm.

Action of Nitrous Acid on β-Phenylethylamine in Hydrochloric Acid Solution.—The amine hydrochloride, precipitated from a benzene solution of the amine by hydrogen chloride, was dissolved in a small quantity of water, and dilute hydrochloric acid added, followed by an aqueous solution of sodium nitrite. The whole was allowed to stand for 2 hours and the reaction was completed by 30 minutes' heating on the water-bath. The oil was extracted with ether, washed, dried, and distilled, the lowest fraction, b. p. 82—87°/21 mm., being collected separately. It was a colourless, non-pungent oil, containing hydrolysable chlorine, and when treated with fuming nitric acid at —15° (compare Barger, J., 1909, **95**, 2193) it yielded β-*p*-nitrophenylethyl chloride, m. p. 46—47°, unaltered by admixture with an authentic specimen. When sulphuric acid was employed in place of hydrochloric acid only very small, impure yields were obtained.

As examples of the methods used in scheme (2), the following are given, since the compounds have not been previously described.

m-*Methoxy-ω-nitrostyrene.*—To a vigorously stirred solution of *m*-methoxybenzaldehyde (28 g.) and nitromethane (13 g.) in alcohol (40 c.c.), 25% methyl-alcoholic potassium hydroxide (23 c.c.) was slowly added, followed by a solution of sodium hydroxide (4 g. in 20 c.c. of water), after which the almost solid product was poured into ice-water and, when *completely in solution*, decomposed with the calculated quantity of ice-cold sulphuric acid; the crude yellow m-*methoxy-ω-nitrostyrene* was filtered, washed, and dried. It crystallised from alcohol in light yellow plates, m. p. 93—94° (Found: N, 8·0. $C_9H_9NO_3$ requires N, 7·8%).

The nitrostyrene (13 g.) was mixed with zinc dust (13 g.) and the mixture added to a vigorously stirred solution of 25 c.c. of glacial acetic acid in 65 c.c. of alcohol, the temperature being kept at 35°. After 10 minutes, alcohol (20 c.c.) was added, and when the temperature had fallen to 15° the solid was filtered off and extracted with ether; the extract was washed with aqueous sodium carbonate and then extracted with sodium hydroxide. m-*Methoxyphenylacetaldoxime* was precipitated from this on the addition of sodium bicarbonate, and was filtered, washed, dried, and recrystallised from ligroin, and finally from water; white needles, m. p. 92·5—93° (Found: N, 8·5. $C_9H_{11}NO_2$ requires N, 8·5%).

From this oxime in alcoholic acetic acid only a very small quantity of β-*m*-methoxyphenylethylamine could be obtained by the action of 3% sodium amalgam.

Action of Phosphorus Pentabromide on β-o-*Methoxyphenylethyl Alcohol.*—*o*-Bromoanisole, b. p. 220°/744 mm., prepared by the action of methyl sulphate on *o*-bromophenol, was converted into β-o-*methoxyphenylethyl alcohol* in the manner already described (Shoesmith and Connor, *loc. cit.*). It is a colourless liquid, b. p. 130—131°/11 mm. (Found: C, 71·8; H, 7·77. $C_9H_{12}O_2$ requires C, 71·1; H, 7·9%). The alcohol (10 g.) was slowly added to phosphorus pentabromide (35 g.) in dry benzene (50 c.c.), the whole being cooled in ice-water. After 30 minutes, dry air was slowly drawn through the solution for 4 hours during which time the pentabromide slowly disappeared. The solution was then washed with ice-water, dried, the benzene distilled, and the residue fractionated under diminished pressure. No definite fraction could be separated other than one at 160—165°/12 mm., which solidified and crystallised from alcohol in fine, non-pungent, white needles of β-5-*bromo*-2-*methoxyphenylethyl bromide*, m. p. 55° [Found: C, 36·9; H, 3·5; Br (total), 53·7; Br (hydrolysable), 27·2. $C_9H_{10}OBr_2$ requires C, 36·7; H, 3·4; Br (total), 54·4; Br (hydrolysable), 27·2%].

The compound resisted oxidation with alkaline permanganate but was oxidised finally according to the scheme $CH_2R{\cdot}CH_2Br \xrightarrow[KOH]{alc.} CHR{:}CH_2 \xrightarrow[+H_2SO_4]{K_2Cr_2O_7} R{\cdot}CO_2H$. Approximately 0·5 g. of the bromide was heated on the water-bath for 30 minutes with 5 c.c. of 20% alcoholic potassium hydroxide; the whole was diluted with water, extracted with ether, the ether distilled, and the residue boiled for 3 hours with 1·2 g. of potassium dichromate and 7 c.c. of 20% sulphuric acid; the resinous oxidation product was separated and boiled with aqueous sodium hydroxide, excess of dilute hydrochloric acid was added, the liberated acid was extracted with ether, and the ether solution in turn extracted with sodium carbonate, from which on acidification and ether-extraction an acid was obtained. Recrystallised from water, it had m. p. 118—119°. 5-Bromo-2-methoxybenzoic acid has m. p. 119° (compare *Gazzetta*, 1886, **16**, 408). This established the constitution of the bromide as above.

Action of Phosphorus Pentabromide on β-m-*Methoxyphenylethyl Alcohol.*—*m*-Bromonitrobenzene was reduced to *m*-bromoaniline by West's method (J., 1925, **127**, 994) and converted into *m*-bromophenol (compare B.P. 200714)—for the necessary details of this process we are greatly indebted to Dr. H. H. Hodgson. This phenol with methyl sulphate gave *m*-bromoanisole, b. p. 214°/729 mm.,

which was then converted into β-m-*methoxyphenylethyl alcohol* in the usual manner. The alcohol is a colourless liquid, b. p. 135—137°/12 mm. (Found : C, 71·1 ; H, 7·6%).

When the alcohol was treated with phosphorus pentabromide, as in the previous case, no definite fraction could be separated, but when excess of pentabromide was used in the cold, a colourless, non-lachrymatory, non-pungent oil, b. p. 163—165°/13 mm., was isolated [Found : Br (total), 53·8 ; Br (hydrolysable), 27·2%]. The compound was oxidised much more readily than its isomeride, and gave an acid, m. p. 160—161°, which did not depress the m. p. of an authentic sample of 6-bromo-3-methoxybenzoic acid (J., 1925, **127**, 880), kindly supplied by Dr. H. H. Hodgson. This characterised the oil as β-6-*bromo*-3-*methoxyphenylethyl bromide*.

Action of Phosphorus Pentabromide on β-p-*Methoxyphenylethyl Alcohol.*—The alcohol was obtained from *p*-bromoanisole in the usual manner, and when purified had b. p. 138—140°/11 mm., m. p. 24° (compare Grignard, *loc. cit.*). When 1 mol. of pentabromide was used per mol. of alcohol, a colourless oil, b. p. 130—131°/11 mm., was obtained, which was almost pure β-p-*methoxyphenylethyl bromide* [Found : Br (hydrolysable), 35·0. $C_9H_{11}OBr$ requires Br (hydrolysable), 37·2%]. It was non-pungent and non-lachrymatory, and very similar in properties to the β-tolylethyl bromides (Shoesmith and Connor, *loc. cit.*), but further fractionation produced no improvement in the quality of the sample. With excess of pentabromide a colourless oil of b. p. 187—188°/19 mm. was formed [Found : Br (hydrolysable), 27·0%]. From this oil an acid of m. p. 217° was obtained on oxidation. 3-Bromo-4-methoxybenzoic acid has m. p. 218° (Balbiano, *Gazzetta*, 1881, **11**, 406), and the oil was therefore β-3-*bromo*-4-*methoxyphenylethyl bromide*.

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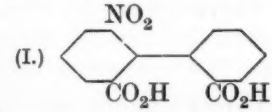
CCXCVIII.—*Investigations in the Diphenyl Series. Part VII. The Relative Stability of Optically Active Diphenic Acids.*

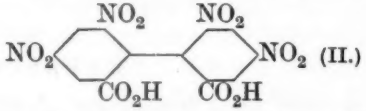
By FRANK BELL and PERCY HARRY ROBINSON.

THE theory advanced to account for the asymmetry of certain diphenyl derivatives (Part VI, this vol., p. 1695; *J. Soc. Chem. Ind.*, 1926, **45**, 864) definitely indicates that the optical activity

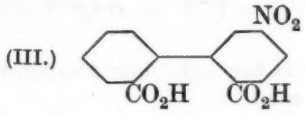
of such compounds should gain in permanence with an increase in the number of groups in the central positions. Up to the present, it has not proved possible to prepare in an optically active condition a compound with only two central groups, although some of the alkaloidal salts of "non-resolvable" acids show marked heterogeneity (compare Christie and Kenner, J., 1923, **123**, 779; 1926, 470).

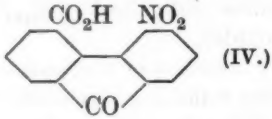
It is now found that 6-nitrodiphenic acid (I) is very much less optically stable than 4 : 4′ : 6 : 6′-tetranitrodiphenic acid (II). Thus



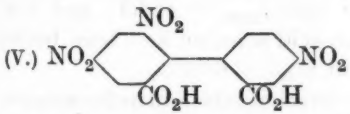


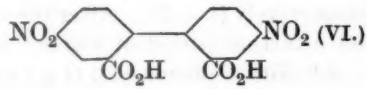
an aqueous solution of the sodium salt of the former acid steadily falls in rotatory power, whilst no such change can be perceived in the case of the latter acid. Further, boiling acetic anhydride racemises 6-nitrodiphenic acid in a very short time, whilst 4 : 4′ : 6 : 6′-tetranitrodiphenic acid loses only 25% of its activity after boiling with acetic anhydride for 10 hours. The failure which has attended attempts to resolve 5-nitrodiphenic acid (III) and 2 : 2′-dinitrodiphenyl-4 : 4′-dicarboxylic acid could have been anticipated from





the "obstacle" theory. It may be noted that 5-nitrodiphenic acid readily forms an *anhydride*, and with sulphuric acid easily undergoes condensation to form a *fluorenone* derivative, in marked contrast to 4 : 4′ : 6′-trinitrodiphenic acid (V) which is unaffected

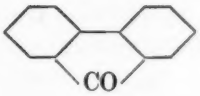
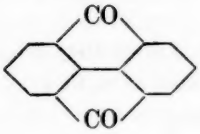




by sulphuric acid at 160°. 4 : 4′-Dinitrodiphenic acid (VI) also does not undergo fluorenone formation (Underwood and Kochmann, *J. Amer. Chem. Soc.*, 1924, **46**, 2069).

Although the failure to resolve fluorenone-4-carboxylic acid has been already reported by Mills, Palmer, and Tomkinson (J., 1924, **125**, 2365), it appeared possible that the introduction of a nitro-group in position 5 might stabilise the enantiomorphous forms which arise if the fluorene system is non-planar. However, 5-nitrofluorenone-4-carboxylic acid (IV) was not resolved by crystallisation of its morphine or quinidine salts, and this result can be interpreted

as indicating that the 4 : 5-positions of fluorene are farther apart than are the 6 : 6′-positions in a diphenic acid. This conclusion agrees with the fact that, although such systems as (VII) are readily formed, attempts to prepare compounds of type (VIII) have repeatedly failed (see Meyer, Meyer, and Taeger, *Ber.*, 1920, **53**, 2034).

(VII.)  (VIII.) 

Experimental.

d- *and* l-6-*Nitrodiphenic Acids.*—The normal quinine salt of 6-nitrodiphenic acid was systematically crystallised from alcohol until it was separated into a slightly less soluble salt, $[\alpha]_{5461}$ + 286·6° ($c = 2{\cdot}5$ in chloroform), and a slightly more soluble salt, $[\alpha]_{5461}$ − 122·4° ($c = 2{\cdot}5$ in chloroform). The former on decomposition gave the *d*-acid with $[\alpha]_{5461}$ + 65·2° ($c = 3{\cdot}01$ in ethyl alcohol), whilst the latter gave the *l*-acid with $[\alpha]_{5461}$ − 66·4° ($c = 4{\cdot}91$ in ethyl alcohol). The *l*-acid had $[\alpha]_{5461}$ + 433° ($c = 4{\cdot}69$ in 0·261*N*-sodium hydroxide), whilst the *d*-acid, obtained from its morphine salt, had $[\alpha]_{5461}$ − 434° ($c = 4{\cdot}73$ in 0·426*N*-sodium hydroxide).

The solution of the sodium salt was kept at room temperature, and the following observations were made :

Time (days)	0	2	9	23	36·5	51
α_{5461}	−20·51°	−18·61°	−14·42°	−8·23°	−4·00°	−1·50°

Solutions of *d*-6-nitrodiphenic acid (1 g.) in 10 c.c. of acetic acid and in 10 c.c. of acetic anhydride were boiled under similar conditions for 1 hour, and they then had α_{5461} + 11·55° and 0·0° respectively ($l = 2$). After the acetic acid solution had been boiled for a further period of 5 hours, it had α_{5461} + 0·94°.

d-6-Nitrodiphenic acid (1 g.) was converted into 5-nitrofluorenone-4-carboxylic acid (see below). The acid obtained was inactive ($c = 2{\cdot}4$; $l = 2$).

l-6-Nitrodiphenic acid was dissolved in excess of thionyl chloride and the solution evaporated in a vacuum. The residue was crystallised from benzene–light petroleum and gave the *l* + *dl*-acid dichloride, m. p. 65—68°, $[\alpha]_{5461}$ − 209·5° ($c = 5{\cdot}04$; $l = 2$), whilst the mother-liquor on evaporation gave a further crop of the dichloride with $[\alpha]_{5461}$ − 220·6° ($c = 2{\cdot}31$; $l = 2$ in chloroform).

d- *and* l + dl-4 : 4′ : 6 : 6′-*Tetranitrodiphenic Acids.*—Boiling alcoholic solutions of tetranitrodiphenic acid (35·7 g. in 1 l.) and

quinidine (30·5 g. in ½ l.) were mixed, and the precipitated salt was filtered off and boiled with alcohol until the residue attained constant rotatory power $[\alpha]_{5461}$ + 243·5° (c = 2·15 in 14·7N-acetic acid); m. p. 252° (decomp.). The alcoholic filtrates were evaporated, the residue was dissolved in acetic acid, and the resultant solution poured into dilute hydrochloric acid. The liberated tetranitrodiphenic acid was extracted with ether, and the well-washed extract dried with sodium sulphate and evaporated. The residue ($[\alpha]_{5461}$ *ca.* − 50°) was boiled with benzene, and the more soluble material was repeatedly crystallised from benzene until it attained constant rotatory power. *l* + *dl*-Tetranitrodiphenic acid formed needles which, after being heated at 130° for ½ hour, melted at 224—226° and had $[\alpha]_{5461}$ − 138·5° (c = 1·7 in ethyl alcohol). The less soluble quinidine salt was decomposed (*a*) by dissolving it in acetic acid and pouring the solution into dilute hydrochloric acid, (*b*) by dissolving in pyridine and pouring the solution into dilute ammonia, (*c*) by grinding with concentrated hydrochloric acid. The acids, recovered as described above and dried at 140°, had almost the same rotatory power, showing that racemisation does not occur during the recovery process.

d-4 : 4′ : 6 : 6′-Tetranitrodiphenic acid, m. p. 226—227° (Found : equiv., 211. Calc. : 211) (0·3696 g. in 20 c.c. of ethyl alcohol in a 2 dm. tube) gave :

λ	4359	4602	5461	5790	6708
α	+16·70°	+11·64°	+5·26°	+4·12°	+2·58°

whence $[\alpha]_{5461}$ +142·3°.

0·4209 G. in 20 c.c. of 1·033N/10-NaOH in a 2 dm. tube gave :

λ	4359	4602	5106	5218	5461
α	+29—31°	+19·6—20·0°	+10·84°	+9·72°	+8·00°

λ	5790	5896	6104	6708
α	+6·33°	+5·86°	+5·08°	+3·78°

whence $[\alpha]_{5461}$ + 190·5°.

After 39 days, this solution had α_{5461} + 8·08°.

A solution of *d*-tetranitrodiphenic acid in acetic anhydride (1 g. in 10 c.c.), with α_{5461} + 23·15°, had after 2 hours' boiling α_{5461} + 18·14°, and after 9 hours' boiling α_{5461} + 17·12°.

l-Tetranitrodiphenic acid was dissolved in thionyl chloride by boiling for 2 hours under reflux, and the solution was evaporated in a vacuum. The residue was difficultly soluble and melted indefinitely. Though no product was isolated in a pure condition, the optical activity was preserved, since $[\alpha]_{5461}$ − 133° (c = 2 in pyridine).

5-Nitrodiphenic acid was prepared by the process described by

Schmidt and Lumpp (*Ber.*, 1908, **41**, 4315). After 1 hour's boiling with acetic anhydride, the solution on cooling deposited crystals of *5-nitrodiphenic anhydride*, m. p. 193—195° (Found: C, 62·4; H, 2·9. $C_{14}H_7O_5N$ requires C, 62·4; H, 2·6%). 5-Nitrodiphenic acid (1·5 g.) in sulphuric acid (5 c.c.) was heated at 160° for ¼ hour, and after cooling poured into water. The precipitated *6(?)-nitrofluorenone-4-carboxylic acid* melted at 282° after crystallisation from acetic acid (Found: equiv., 270·5. $C_{14}H_7O_5N$ requires equiv., 269). 5-Nitrodiphenic acid gave non-crystallisable quinine, morphine, and quinidine salts. The brucine salt on crystallisation from water gave successive crops with $[\alpha]_{5461}$ — 10·4°, — 10·9°, — 11·2°, —11·1° ($c = 2·5$; $l = 2$ in 14·7*N*-acetic acid), indicating that no resolution had taken place.

5-Nitrofluorenone-4-carboxylic acid was prepared by the method of Moore and Huntress (*J. Amer. Chem. Soc.*, 1927, **49**, 1324). The quinidine salt showed slight irregularity in rotatory power ($[\alpha]_{5461}$ *ca.* — 20·6°; $c = 2·5$ in chloroform) but no resolution was effected. The morphine salt was crystallised from alcohol and showed a constant rotatory power of $[\alpha]_{5461}$ — 73·5° ($c = 2$ in 14·7*N*-acetic acid).

2 : 5 : 7(?)-*Trinitrofluorenone-4-carboxylic acid*, obtained by heating 5-nitrofluorenone-4-carboxylic acid (2·5 g.) with nitric acid (*d* 1·5; 50 c.c.) at 100° for 2 hours, pouring into water, and crystallising the resulting mass from aqueous alcohol, forms glistening, pale yellow plates, m. p. 254—255° (Found: C, 46·5; H, 1·7. $C_{14}H_5O_9N_3$ requires C, 46·8; H, 1·4%).

2 : 2′-Dinitrodiphenyl-4 : 4′-dicarboxylic acid was prepared from 4-bromo-3-nitrobenzoic acid. Its excessive insolubility militated against the production of uniform normal alkaloidal salts. The brucine salt on crystallisation from water varied in rotatory power between $[\alpha]_{5461}$ — 40° and $[\alpha]_{5461}$ — 56° ($c = 2$ in pyridine), but the liberated acid was inactive when observed in 1·033*N*/10-sodium hydroxide.

Quinine salts of 4-nitrodiphenic acid. An alcoholic solution of quinine (2 mols.) and 4-nitrodiphenic acid (1 mol.) was allowed to crystallise slowly. Successive crops had $[\alpha]_{5461}$ + 94·4°, + 84·0°, + 77·2° ($c = 2·5$ in chloroform), and the mother-liquor on evaporation and desiccation gave a solid with $[\alpha]_{5461}$ + 11·9°. Recrystallisation of the intermediate crops raised the rotatory power to $[\alpha]_{5461}$ + 106·4°; m. p. 180° (indefinite) (Found: C, 66·3; H, 5·6%). The liberated 4-nitrodiphenic acid was inactive in every case. The difference in rotatory power may be attributed to: (*a*) resolution of the alkaloidal salt; (*b*) admixture of acid and normal quinine salts and quinine; (*c*) differences in the number of

molecules of solvent of crystallisation—none of the salts lost more than 0·5% by weight on drying for 1 hour at 120°, however; or (*d*) possible presence of 6-nitro- and 4 : 4′-dinitro-diphenic acids as impurities.

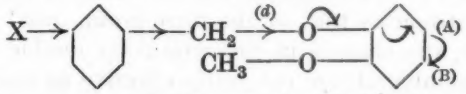
In conclusion, the authors wish to express their thanks to the Department of Scientific and Industrial Research for a grant made to one of them.

BATTERSEA POLYTECHNIC, S.W. 11. [*Received, July 6th*, 1927.]

CCXCIX.—*The Relative Directive Powers of Groups of the Forms* RO *and* RR′N *in Aromatic Substitution. Part VI. The Nitration of* m- *and* p-*Chlorobenzyl Ethers of Guaiacol.*

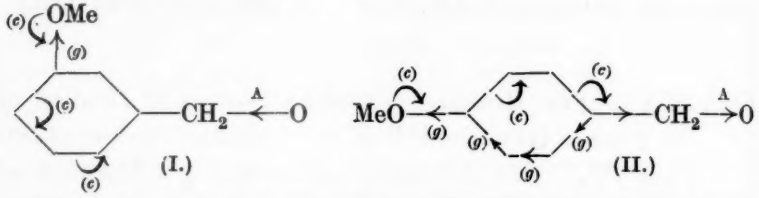
By ALBERT EDWARD OXFORD and ROBERT ROBINSON.

IN studying the relative directive powers of substituted benzyloxy-groups, we examine, in effect, the influence of the modified benzyl group on the electrons of the oxygen atom, and an important feature of the method is that the reactive centres are spatially removed from the benzyl group. The annexed diagram serves to illustrate this point, and just as Flürscheim secured a more just comparison of groups by excluding for certain purposes the ortho-derivatives, so we imagine that the device of relaying the effects of a group and estimating them at a distant point in the molecule constitutes a further step in the same direction.



In the case represented, X and also X·C_6H_4 are hypothetical kations that have a smaller electron affinity than a proton: this produces an electron displacement (*d*) in the sense indicated and relative to the mean positions of electrons in the corresponding position in the methoxy-group. The contiguous oxygen atom and the associated crotenoid system are thus stimulated, and the velocity of substitution at (B) is greater than that at (A). Groups are compared by putting them separately into competition with methoxyl, and in Part II (J., 1926, 383) it was shown in this way that the directive powers of the *m*-nitrobenzyloxy- and *p*-nitrobenzyloxy-groups are approximately equal (67; MeO = 100). Similarly, the directive power of the *m*-methoxybenzyloxy-group was found to be 92, indicating that in the absence of conjugative

disturbances, admittedly never completely eliminated in the formal systems, the methoxyl group must be regarded as one that has a greater electron affinity than hydrogen (I; resultant effect $g>c$ at A). Unfortunately, the directive power of the *p*-methoxybenzyloxy-group could not be determined; we had anticipated a considerably augmented value (>113, the directive power of the benzyloxy-group) as the result of the combined conjugative and general effect shown in (II) ($c>g$ at A).



The chlorine atom has a greater electron affinity than the methoxyl group, implying an increased general effect and a decreased conjugative effect, and the theoretical disparity between the directive powers of *m*- and *p*-chlorobenzyloxy-groups is thus smaller than that which should exist between the directive powers of the *m*- and *p*-methoxybenzyloxy-groups. Actually, we find that *m*-chlorobenzyloxy- has the directive power 69, and *p*-chlorobenzyloxy- 82. In both cases, therefore, the general effect of chlorine is paramount, but the higher value for the para-derivative is in harmony with our theoretical anticipations, and is probably due to crotenoid conjugation analogous to that symbolised in (II). The close approach of the directive power of *m*-chlorobenzyloxy- to that of *m*-nitrobenzyloxy-, showing that the electron affinity of chlorine is almost as strong as that of the nitro-group, need not occasion surprise, since the charges in the semi-polar double bonds, often assumed to be integral, are not really effective as such on account of the distortion and polarisation of the atoms that must enfeeble their external fields. It is probable that the difference between Cl and NO_2 lies not so much in their respective electron affinities as in the circumstance that Cl possesses free electrons, whereas the N of NO_2 does not. Therefore in C–Cl there may be occasional phases, non-existent in the case of C–NO_2, in which the co-valency with the carbon atom is increased, or alternatively, in which the electron density in the neighbourhood of the carbon atom is increased by the chlorine atom to such an extent that a co-valency change would occur if an electron-seat were available. The C–Cl group is thus the more plastic, and the electric intensity of the external fields varies over a greater range. This condition would be sufficient to account for such facts as the predominating *op-*

substitution of $Ph{\cdot}CH_2{\cdot}Cl$ as compared with the *mp*-substitution of $Ph{\cdot}CH_2{\cdot}NO_2$, even although the *average* electron affinities of Cl and NO_2 were approximately equal. The method of examination through a relay atom overcomes this difficulty to a large extent, because the phases at the C–Cl group that favour the reaction examined cannot be effective unless they happen to synchronise with a phase of the relay atom ($\overset{\curvearrowright}{O}\!-\!C$ in the cases considered in this communication) also promoting reaction. It is obvious that this requirement must augment the relative importance of the normal conditions and diminish the magnitude of effects of the infrequent phases, $C\!-\!\overset{\curvearrowleft}{Cl}$ and $C\!\leftarrow\!Cl$.

Experimental.

Shoesmith and Slater (J., 1926, 219) obtained *m*-chlorobenzyl bromide, b. p. 109°/10 mm., from *m*-nitrobenzaldehyde through *m*-chlorobenzaldehyde and *m*-chlorobenzyl alcohol, which was treated with hydrogen bromide in benzene solution. We have employed two methods: (*A*) Aceto-*p*-toluidide ⟶ 3-chloro-*p*-toluidine (Chattaway and Orton, J., 1900, **77**, 792) ⟶ 2-chloro-4-methylphenylhydrazine ⟶ *m*-chlorotoluene ⟶ *m*-chlorobenzyl bromide (by refluxing with the theoretical amount of bromine). (*B*) *m*-Nitrobenzyl alcohol ⟶ *m*-aminobenzyl alcohol (Lutter, *Ber.*, 1897, **30**, 1065) ⟶ *m*-chlorobenzyl alcohol (in excellent yield) ⟶ *m*-chlorobenzyl bromide (by means of bromine and red phosphorus, compare Part II, *loc. cit.*). Both processes yielded an oil, b. p. 120—123°/24—25 mm., and the specimens were identified by conversion into 5-nitro-2-*m*-chlorobenzyloxyanisole, m. p. 121°. A mixture of the two specimens melted at the same temperature.

p-Chlorobenzyl bromide was obtained by the bromination of *p*-chlorotoluene (44 g.) (Jackson and Field, *Ber.*, 1878, **11**, 905). After crystallisation from 85% alcohol, 15 g. of nearly colourless needles, m. p. 50°, were obtained (Shoesmith and Slater, *loc. cit.*, give m. p. 51°). The following guaiacol and nitroguaiacol ethers were prepared by methods closely resembling those employed previously (Part II, *loc. cit.*) for the corresponding *m*- and *p*-nitrobenzyloxy-derivatives. The crude products never melted more than 1° lower than the true m. p., but were recrystallised two or three times, a process which did not alter the m. p.'s.

2-m-*Chlorobenzyloxyanisole*, $MeO{\cdot}C_6H_4{\cdot}O{\cdot}CH_2{\cdot}C_6H_4Cl$, b. p. 207—208°/15 mm., crystallised from light petroleum in slender needles, m. p. 46—47° (Found: C, 67·2; H, 5·4. $C_{14}H_{13}O_2Cl$ requires C, 67·6; H, 5·3%). It is readily soluble in most organic solvents.

4-*Nitro*-2-m-*chlorobenzyloxyanisole*, $MeO{\cdot}C_6H_3(NO_2){\cdot}O{\cdot}CH_2{\cdot}C_6H_4Cl$,

crystallises from alcohol in minute, slender, colourless needles, m. p. 129—130·5° (Found: Cl, 12·3. $C_{14}H_{12}O_4NCl$ requires Cl, 12·1%).

5-*Nitro*-2-m-*chlorobenzyloxyanisole* crystallises from alcohol in colourless, feathery needles, m. p. 121° (Found: C, 57·0; H, 4·4. $C_{14}H_{12}O_4NCl$ requires C, 57·2; H, 4·1%).

2-p-*Chlorobenzyloxyanisole* crystallises from methyl alcohol in colourless, rectangular prisms, and from light petroleum in large, very well-defined prisms, m. p. 70° (Found: Cl, 14·3. $C_{14}H_{13}O_2Cl$ requires Cl, 14·3%). A description of these (Fig. 1) is contributed by Mr. H. E. Buckley, of the Crystallography Department of this University.

FIG. 1.

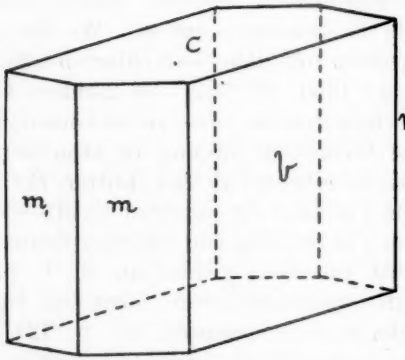
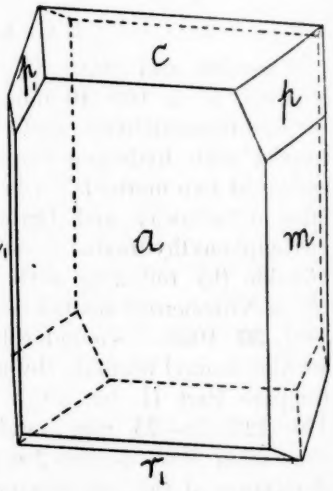


FIG. 2.



Symmetry: rhombic. Axial ratios: $a : b : c = 0{\cdot}7054 : 1 : 0{\cdot}7013$. Forms developed: b(010, tabular), c(001), m(110); (011) is very rare. Mean angular values: 011—001, 35° 3′ (6 angles; limits, 35° 0′—35° 12′); 010—110, 54° 48′ (24 angles; limits, 54° 35′—55° 1′). Cleavage: imperfect, parallel to 100.

4-*Nitro*-2-p-*chlorobenzyloxyanisole* crystallises from alcohol in colourless, lustrous, feathery needles, m. p. 115—117° (Found: Cl, 11·8%).

5-*Nitro*-2-p-*chlorobenzyloxyanisole* crystallises from alcohol in colourless, flat needles, m. p. 120—120·5° (Found: Cl, 12·0%). Mr. Buckley has kindly examined the crystals (Fig. 2) deposited on slow evaporation of a solution in light petroleum.

System: monoclinic prismatic. Axial ratios: $a : b : c = 2{\cdot}699 : 1 : 1{\cdot}708$. $\beta = 74°\ 40'$. Habit: somewhat tabular on a(100). Forms generally developed: a(100), m(110), $r(\bar{1}01)$, c(001),

and *p*(111). Mean angular values (calculated values in parentheses): *ac* 74° 40′, *am* 68° 59′, *ra* 69° 5′, *mc* 84° 37′ (84° 33′), *mr* 36° 15′ (36° 15′), *m* (110) *m*′ ($1\bar{1}0$) 42° 3′ (42° 3′), *pc* 56° 12′ (56° 1′).

Mixtures of 4- *and* 5-*Nitro*-2-m-*chlorobenzyloxyanisoles*.—The following freezing points were observed, the first number of each pair indicating the % of the 5-nitro-isomeride in the mixture: 15·36, 123·7° (1); 22·62, 119·85° (2); 30·42, 115·05° (3); 38·09, 110·0° (4); 43·12, 106·0° (5); 46·34, 103·65° (6).

Nitration of 2-m-*Chlorobenzyloxyanisole*.—The conditions given for the nitration of 2-*p*-nitrobenzyloxyanisole (Part II, *loc. cit.*, p. 389) were followed exactly. 1·7214 G. of the ether gave 2·0119 g. of the dried nitration product (yield, 99·0%), which was almost colourless and melted to a transparent liquid only slightly darker than that formed on fusion of the pure nitro-ethers. The filtrate and washings from the nitration were colourless and gave no coloration on the addition of sodium hydroxide. Since this product was found to behave as a binary mixture, it was not considered necessary to purify it by washing with methyl alcohol or in any other way. The f. p. of the nitration product was 107·55°, and from the graph we find: 5-nitro-isomeride, 41·1% [the Lagrange interpolation formula gave 41·3%, from points (2) to (5) inclusive]. A mixture of the nitration product (1·3779 g.) and the 4-nitro-isomeride (0·4796 g.) had f. p. 115·1°, practically coinciding with point (3) (30·42% of the 5-nitro-isomeride) and showing 40·9% of the 5-nitro-isomeride in the nitration product. A mixture of the nitration product (1·3779 g.) and the 4-nitro-isomeride (0·7884 g.) froze at 117·9° (5-nitro-isomeride, 25·95% from the graph), giving 40·8% of the 5-nitro-isomeride in the nitration product. A mixture of the 5-nitro-isomeride (0·6151 g., 41%) and of the 4-nitro-isomeride (0·8865 g.) froze at 107·8°, whilst the addition of 4-nitro-isomeride (0·5494 g.), reducing the 5-nitro-isomeride to 30·0%, raised the f. p. to 115·4°. These observations confirm those used in constructing the graph, and it appears that the nitration product contains 41% of the 5-nitro-isomeride. Hence the directive power of the *m*-chlorobenzyloxy-group is 69·5 (MeO = 100).

Mixtures of 4- *and* 5-*Nitro*-2-p-*chlorobenzyloxyanisoles*.—The following freezing points were observed, the first number of each pair indicating the % of the 5-nitro-isomeride in the mixture: 0, 116·3° (1); 9·8, 111·25° (2); 20·48, 106·0° (3); 32·26, 99·25° (4); 36·73, 95·6° (5); 44·86, 89·55° (6); 49·82, 84·8° (7). In (7) the first f. p. was 84·8°; the temperature then fell to 84·6°, and gradually rose to 86·05°, at which it remained constant for several minutes. This behaviour indicates the formation of an equimolecular compound of the components.

Nitration of 2-p-*Chlorobenzyloxyanisole.*—Except for the numerical details, the remarks made above on the *m*-isomeride are applicable to this case in every respect. (*a*) 1·9816 G. gave 2·3169 g. of the dried nitration product (yield, 99·0%) (Found : C, 57·1; H, 4·1. Calc. for $C_{14}H_{12}O_4NCl$: C, 57·2; H, 4·1%). (*b*) 1·2848 G. gave 1·4942 g. (yield, 98·5%). Nitration product (*a*) froze at 89·15°, (*b*) at 89·0°, and the f. p. 89·1° corresponds on the graph to 45·4% of the 5-nitro-isomeride. Mixtures of the nitration product (1·4424 g.) with the 4-nitro-isomeride (0·3487 g. and 0·6065 g.) had f. p.'s 96·0° and 99·55°, respectively. Both these values are very close to determined points (5 and 4 respectively) : the first corresponds to 36·24% of the 5-nitro-isomeride, giving 45·0% of this in the nitration product, and the second to 31·74% of the 5-nitro-isomeride, giving 44·8% in the nitration product. The f. p. of a mixture of the 5-nitro-isomeride (0·7226 g., 44·85%) and the 4-nitro-isomeride (0·8884 g.) was 89·2°. Hence the nitration product contains 45% of the 5-nitro-isomeride, and the directive power of the *p*-chlorobenzyloxy-group is 82 (MeO = 100).

THE UNIVERSITY, MANCHESTER. [*Received, July 20th,* 1927.]

CCC.—*The Thermal Dissociation of Carbonyl Chloride.*

By HORACE INGLESON.

THE object of the present work was to obtain satisfactory values for the dissociation constant of a chemical change. As carbonyl chloride dissociates at temperatures sufficiently low to admit of accurate determinations being made, it was decided to study this particular change. Reference to the literature showed serious differences in the results of investigators prior to 1921; these results are summarised in Table I. At the lower temperatures, the values are in bad agreement. Thus, an approximate calculation shows that the value at 341° obtained by extrapolation from Horak's data (Diss., Berlin, 1909) would be of the order of 4000, and not 8280 as calculated from the results of Atkinson, Heycock, and Pope (J., 1920, **117**, 1410). At the higher temperatures, there is a similar lack of agreement among different workers : in nearly every case the results of Atkinson, Heycock, and Pope correspond to a smaller degree of dissociation than that found by other workers.

Bodenstein and Dunant (*Z. physikal. Chem.*, 1908, **61**, 437) used the streaming method in their experiments, and determined the equilibrium both from the thermal combination of carbon monoxide and chlorine and from the dissociation of carbonyl chloride. They

concluded that their results confirmed the theory of Nernst as well as could be expected in the absence of values for the specific heat of carbonyl chloride. Horak (*loc. cit.*) used a quartz spiral manometer in order to measure the pressure developed in a heated porcelain tube filled with the gas, whereas Atkinson, Heycock, and Pope (*loc. cit.*) applied the streaming method to measure the extent of the thermal dissociation of the gas in the presence of a catalyst at temperatures between 101° and 517°.

During the progress of the present work, Christiansen (*Z. physikal. Chem.*, 1922, **103**, 99) published the results of an investigation of the factors affecting the velocity of decomposition of the gas at different temperatures. He concluded that the decomposition was accelerated by the chlorine produced, but his work gives very little information concerning the dissociation constants.

In 1924, Bodenstein and Plaut (*Z. physikal. Chem.*, **110**, 399) described experiments made at temperatures between 373° and 451°, and their results are included in Table I. They were able to confirm the observation of Christiansen that the chlorine accelerates the decomposition.

TABLE I.

Data at present available.

Temp.	K_c.	Author.*	Temp.	K_c.	Author.*	Temp.	K_c.	Author.*
603°	15·0	B.D.	460°	298·7	A.H.P.	404°	1123·0	H.
553	38·0	B.D.	451·3	264·8	B.P.	400	954·6	A.H.P.
506	612·5	A.H.P.	450	343·9	H.	399	1365·0	H.
505	379·0	A.H.P.	449	425·0	A.H.P.	394·6	1230·0	B.P.
505	105·4	A.H.P.	444·1	348·2	I.	389	1409·0	I.
503	78·2	B.D.	443	419·1	A.H.P.	384	2054·0	H.
500	137·5	H.	425	630·7	H.	373·3	1884·0	B.P.
486	209·5	A.H.P.	415	717·9	I.	357	3654·0	I.
481·4	151·6	I.	413·6	719·5	B.P.	341	8281·0	A.H.P.
475	223·9	H.	406	1414·0	A.H.P.			

* B.D. Bodenstein and Dunant. A.H.P. Atkinson, Heycock, and Pope. B.P. Bodenstein and Plaut. I. Ingleson (present paper). H. Horak.

Preliminary Experiments at the Boiling Point of Sulphur.

1. *Chemical Series.*—From a consideration of the difficulties inherent in the streaming method, it seemed likely that some modification of the static method would be more suitable for carrying out the experiments. In the first series of eight experiments, which gave a mean value of $K_c = 354$, a known weight of carbonyl chloride was heated in a closed, thin-walled bulb of glass by suspending it in the vapour of sulphur boiling under atmospheric pressure. At the end of 8 hours, the bulb was quickly removed from the heating bath into a rapid current of carbon dioxide; it was shielded from the light, and the chlorine was determined iodometrically.

This series of experiments and later series in which a similar method was used have been called " chemical." It was decided to control these results by a second set of experiments at the same temperature, based on methods which may be termed " physical."

2. *Physical Series.*—In this series, a glass bulb, filled with a known amount of carbonyl chloride, was heated as before, but the pressure corresponding to equilibrium was measured in a manometer containing mercury after the interposition of an " air buffer." This series gave the value $K_c = 364$ as the mean of eight experiments. Since the agreement of the results of the two series at the boiling point of sulphur was satisfactory, the methods were applied at the boiling point of mercury.

Preliminary Experiments at the Boiling Point of Mercury.

1. *Physical Series.*—The experiments were carried out in the manner just described except that a small amount of charcoal was used to accelerate the rate of attainment of equilibrium. The mean of four concordant results was $K_c = 3007$.

2. *Chemical Series.*—On account of the small extent of decomposition, the chlorine determinations were checked by making careful measurements of the amount of carbon monoxide formed. It was found that the percentage decomposition calculated from the determination of the chlorine was smaller in every instance than that derived from the carbon monoxide measurements; *e.g.*, in one experiment the carbon monoxide measurements indicated 9·1% decomposition (corresponding to $K_c = 3249$), whilst 7·8% decomposition ($K_c = 4429$) was calculated from the chlorine determinations. The means of the values from the chlorine and carbon monoxide determinations were, respectively, $K_c = 4350$ and $K_c = 3181$. It will be seen that the value obtained in the physical experiments, $K_c = 3007$, agrees better with the latter than with the former. As it was clear that the chemical method could not be used with advantage, the physical method was modified so that continuous observation of the pressure of the decomposing gas could be made. By this means, it was found possible to establish the cause of the discrepancy between the two sets of results.

3. *Second Physical Series.*—The apparatus used consisted of a reaction vessel of glass which was joined to a U-tube containing concentrated sulphuric acid. By suitable manipulation of a tap, the U-tube could be made to serve as a manometer which protected the mercury in a second manometer from attack by the chlorine produced in the decomposition. The reaction vessel was filled with carbonyl chloride at room temperature to a convenient pressure, and after the heating of the vapour-bath had commenced, the

levels of the acid in the U-tube were maintained nearly constant by gradually increasing the pressure of the air in one limb of the tube. Readings of the pressure of the gases in the bulb were made at regular intervals after the temperature of the bath became constant. It was expected that the pressure would gradually increase to a constant value, the rate of increase slowly falling to zero. It was found, however, that the rate of increase of pressure did not fall to zero, but only decreased to a small constant value even after prolonged heating had taken place. This suggested that the observed rate of change was not determined simply by the dissociation of carbonyl chloride. On removing the bulb from the heating bath, a marked etching of the inner surface was noticed. The white solid which gave the etched appearance showed the reactions of a chloride.

The results of the eight experiments comprising this series gave an average value of $K_c = 3031$, which is in good accord with the results from the chemical determinations of the carbon monoxide ($K_c = 3181$) and from the first physical series ($K_c = 3007$). These three results lend support to the following explanation of the non-equivalence of the chlorine and carbon monoxide in the chemical series. During the prolonged heating, the materials of the bulb were attacked by the chlorine present and evolution of gas took place. The removal of the chlorine caused a disturbance of the equilibrium and further dissociation of carbonyl chloride took place to re-establish it. Thus, analysis by the chemical method gives a quantity of free chlorine which is too small, whilst the amount of gas determined as carbon monoxide is too large. From this it may be concluded that trustworthy results cannot be obtained in experiments in which the gases are heated for long periods in glass bulbs. A bulb of transparent fused quartz was therefore employed in the later experiments.

Later Experiments.

The results obtained in the five series of experiments made at 357°, 389°, 415°, 444·1°, and 481·4° have been summarised in Table I. Experiments were first made in vapour baths at 357° and 444·1°; subsequent experiments were precisely similar except that they were carried out in an electric furnace. Those at 389° and 415° were chosen so as to give nearly equal intervals, and when the results at these four temperatures were plotted it was found that a straight line passing through the points corresponding with 357°, 415°, and 444·1° did not pass exactly through that corresponding with 389°. Further experiments were made at 481·4°, which clearly showed that a straight-line relationship exists between

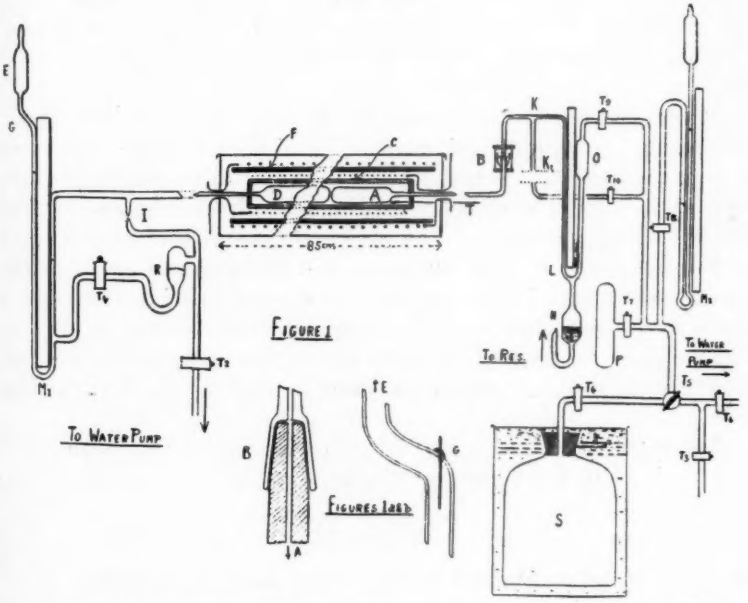
the reciprocals of the temperature and the logarithms of the constants.

Experimental.

The phosgene used throughout was obtained from Kahlbaum in sealed glass bombs. The apparatus is shown in Fig. 1. The quartz bulb, A, had a capacity of about 175 c.c. and was placed inside the heavy copper tube, C. It was joined to the rest of the apparatus through the ground joint, B. This was specially made in order to contain the smallest possible volume (see Fig. 1A), and was lubricated with a thin layer of chlorinated lanoline from which all traces of volatile substances had been removed. The whole was sealed by immersion in mercury, and the two sections of the joint were securely held together. The copper tube was about 65 cm. in length and 5·4 cm. in diameter, and had a wall thickness of 9 mm. Thick copper plates were fixed to the ends of the tube after the bulbs A and D had been placed in position. The tube was evenly wound with heavy gauge nickel-chrome wire, the winding being carried as near to the ends of the tube as possible. The tube F extended beyond the ends of the copper tube for a length of about 8 cm. It reduced the loss of heat from the ends of the copper tube and also kept this tube in an enclosure at a fairly uniform temperature. The tubes were carefully packed in kieselguhr in an iron box. The bulb D was of glass and had a capacity of about 500 c.c. The manometer M_1 carried an evacuated bulb, E, and had a stout platinum wire fused in at G (see Fig. 1B). The T-piece, I, served only in the drying and filling of the bulb, D. The portion of the apparatus just described is called the air-regulator. It served as an air thermometer and also controlled the current supplied to the furnace. The windings round the iron and copper tubes were in parallel and the circuits were so arranged that when that round the copper tube was broken by the operation of the air-regulator, about 2% of the total current was cut off. Fluctuations in the total current caused by changes in the voltage at the laboratory mains were compensated for by the adjustment of a rheostat by hand. This regulation of the current was carried out continuously during the whole time required for an experiment. Observations showed that it was easy to maintain the temperature constant to $\pm$ 0·25° when the temperature of the laboratory was kept fairly constant. The pressure of the carbonyl chloride at room temperature is shown in Tables II and III under the heading p_1. After the pressure of the air in the large bottle, S, had been adjusted to be nearly equal to p_1, the tap, T_4, was closed. The bottle was kept in a well-regulated thermostat. The quartz bulb and all the connecting tubes were repeatedly evacuated and washed

out with the gas before being filled. Air-free, concentrated sulphuric acid was allowed to close the seal, L, and enter O to a convenient height. The pressure of the gas in the quartz bulb was measured on the vacuum-type manometer, M_2. The heights of the mercury in the manometers were read to 0·1 mm. with the aid of a cathetometer. The temperature of the gas was read on a mercury thermometer, T, graduated to 0·1°, which had been checked at the melting point of ice and at the transition point of the system $Na_2CrO_4,10H_2O$–$Na_2CrO_4,6H_2O$–H_2O. After the pressure and temperature of the air in the bulb D had been measured, a nitrogen-filled

FIG. 1.



thermometer was put in position, the tap T_4 was opened and the heating current passed through the furnace. Well-dried air was admitted into S to keep the levels of the acid in the seal nearly stationary and thus compensate for the gradual increase in pressure of the gases in the quartz bulb. During the heating, approximate measurements were made of the pressures of the gases in the bulbs. It was observed that up to about 350° the pressures increased roughly in proportion to their initial values. Then the gases in the quartz bulb began to exert a proportionately greater pressure than did the air in the bulb D. This effect became more and more marked, and the rate of decomposition as deduced from pressure measurements passed through a maximum value after the highest temperature

had been reached. This behaviour is in accord with the observations of Christiansen (*loc. cit.*). When the pressure of the decomposing gas ceased to increase, the experiment was discontinued. Heating of the bulb was in all cases continued for 12—24 hours after chemical equilibrium appeared to have been reached. The pressures corresponding to equilibrium are given in Tables II and III in columns headed p_2.

In order to provide a check upon the high temperatures employed, air was frequently substituted for carbonyl chloride in the bulb A. Measurements of the quantity pv/T for the quartz bulb and the tubing connected to it were made. The value of T at the high temperature was deduced from measurements of the pressures in the air-regulator. As an example of the values found at the low and high temperatures, a determination at 389° is given : pv/T at 19·2° = 157·7 ; pv/T at 389° = 157·5.

In determining the true value of the concentrations of the gases composing the equilibrium mixture, several corrections were introduced. A small amount of carbonyl chloride in the tubing between the furnace and the meniscus of the acid in the seal was exposed either to bright daylight or to an electric lamp, and thus was not at the temperature of the furnace when the final pressure measurements were made. It is evident that if the equilibrium mixture of gases in the hot bulb could be separated from the gas in the cold tubing and then allowed to regain its original composition and temperature of filling, it would not exert a pressure p_1, but a smaller pressure.

The separate series of experiments which gave the mean values shown in Table I are discussed below.

TABLE II.

Results obtained at the boiling point of mercury.

No.	p_1 (mm.).	Temp.	p_2 (mm.).	% Dec.	K_c (corr.).	B. p. (°K.)
19	304·57	16·8°	737·66	12·32	3470	629·2°
20	292·78	14·7	712·8	12·92	3778	629·5
21	305·46	15·2	741·3	11·47	3813	630·1
22	301·44	15·3	732·46	11·89	3766	630·9
23	291·25	14·3	714·0	12·24	3633	630·5
24	299·59	20·6	717·9	12·22	3608	629·6
25	304·77	20·6	730·25	12·30	3512	630·25
					Mean 3654	

Table II gives the results of experiments made at the boiling point of mercury; the alteration of the boiling point with the change n the atmospheric pressure was taken into account. (Data for this correction, and also for that of the series at the b. p. of sulphur, are taken from the *Chemiker Kalender*, 1922, Vol. 2, pp.

129, 130.) The temperature at which each experiment was made is shown in the last column of the table.

It is considered that the results are more trustworthy than any hitherto obtained at 357°. The values of the constant are calculated directly from the percentage decomposition (% Dec.) after the use of the corrections referred to above.

TABLE III.

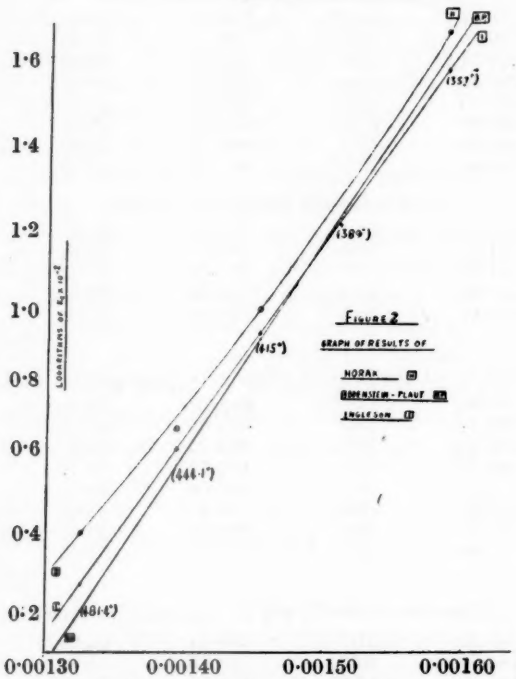
No.	p_1 (mm.).	Temp.	p_2 (mm.).	% Dec.	K_c (corr.).
	(*a*) Results obtained at 388—389°.				
1	271·27	14·9°	748·36	20·55	1248
2	259·5	11·6	722·80	20·36	1319
3	276·34	21·4	747·77	20·46	1118
4	268·89	20·4	729·30	20·63	1273
5	248·23	21·7	667·27	20·34	1432
7	259·87	21·1	703·10	20·56	1352
8	250·76	19·3	680·22	20·22	1423
9	246·06	23·05	662·32	20·79	1373
	(*b*) Results obtained at 415°.				
1	244·80	14·5°	743·10	27·27	720·0
2	231·15	12·6	708·38	27·84	722·1
3	232·20	12·7	710·62	27·71	726·3
4	232·30	12·5	712·90	27·99	707·1
5	231·61	10·5	714·65	27·86	71[illegible]0
					Mean 717·9
	(*c*) Results at the b. p. of sulphur (average temp., 444·1°).				
1	206·80	23·6°	692·15	39·14	357·9
2	196·43	18·4	672·03	40·21	345·2
3	203·43	19·3	691·22	39·57	349·6
4	204·22	21·0	687·14	39·48	353·1
5	203·50	16·8	697·08	39·71	343·7
6	204·28	16·0	706·71	41·38	307·5
7	204·20	16·9	698·01	39·26	353·0
8	210·56	15·7	721·04	39·56	335·1
					Mean 348·2
	(*d*) Results at 480·3°, 481·2°, and 482·5°, respectively.				
1	203·25	21·1°	788·41	52·31	158·2
2	184·78	20·2	729·75	54·40	153·5
3	187·00	17·35	751·93	55·22	143·2
					Mean 151·6

Of the experiments in Table III*a*, Nos. 1—4 were made at 388° and the others at 389°. The mean from Expts. 5—9 is $K_c = 1395$, or, excluding No. 7, $K_c = 1409$. It was found that a trace of sulphuric acid had entered the quartz bulb in Expts. 1—4; the effect of this would be to give too large a final reading of the pressure p_2 and thus too small a value for K_c. Furthermore, since the value $K_c = 1409$, from Expts. 5, 8, and 9, approximates more closely to the smoothed curve representing the results at other temperatures (see p. 2252), this value is regarded as the more trustworthy and is quoted in Table I.

A comparison of the results given in Table IIIc (which all relate to temperatures between 443·7° and 444·8°) with the values obtained in the preliminary experiments at the boiling point of sulphur shows a very satisfactory agreement between the three sets of values.

In the graph shown in Fig. 2 the values of log $K_c/100$ have been plotted against the reciprocals of the corresponding absolute temperatures, the Centigrade temperatures being shown along the

FIG. 2.



Reciprocals of absolute temperature.

course of the graph. The values now found are seen to be approximately intermediate between the most satisfactory values hitherto published. When plotted on a scale sufficiently large to take account of 0·0025 in the logarithms and of 5×10^{-7} in the reciprocals of the temperatures, the points corresponding to the temperatures 481·4°, 444·1°, 415·0°, and 357·0° lie exactly on a straight line. The value of K_c at 389° interpolated from this line is 1429, whereas the experimentally determined value is 1409, *i.e.*, about 1% smaller. There is little doubt that the curves of Horak and of Bodenstein and Plaut point to a value of the constant at 357° which is too

large. It is considered that the author's graph reproduces the values of the constant over a range of 120° with considerable accuracy.

Heat of Reaction.

Thomsen ("Thermochemische Untersuchungen," Vol. II, p. 359), in repeating the work of Berthelot on the heat of the reaction $CO + Cl_2 = COCl_2$, measured both (1) the heat change which occurs when carbonyl chloride is passed into aqueous potassium hydroxide, and (2) the heat evolved by the combustion of a mixture of the gas with hydrogen in an atmosphere of oxygen. Berthelot had used the first method and found a value of 18,000 cals., but Thomsen showed that the true value was much higher and obtained results of 26,620 and 25,650 cals. by the two methods. There is thus a difference of 970 cals. between the values given by Thomsen, the mean being 26,100 cals.

The results now obtained have been used to calculate this heat of reaction (Q_v), which has been assumed to remain constant within each temperature-range shown in Table IV. The range (4*a*) has been included to show the effect upon Q_v and Q_p of using the interpolated value (1429) of K_c at 662° K. instead of the experimental result (1409), which gives the results in range (4). Since Thomsen's data apply at constant pressure at room temperature, the comparison of his results must be made with those shown in col. 3 which are the heats of reaction at constant pressure at the mean temperatures shown in col. 4. The mean of these is 25,500 cals. at an average temperature of 416°, thus differing from Thomsen's mean by 600 cals.

TABLE IV.

Temp. ranges (°K.).	Q_v.	Q_p.	Mean temp., °K.
(1) 754·4—717·1	24,030	25,500	735·7
(2) 717·1—688	24,530	25,930	702·6
(3) 688—630	24,340	25,660	659
(4) 688—662	23,620	24,970	675
(4*a*) 688—662	24,100	25,450	675

It appears doubtful whether this difference between the two values has any real significance as it is within the limits of experimental error in Thomsen's results.

Summary.

The values found by different authors for the dissociation constant of carbonyl chloride show wide divergences, and experiments have therefore been made over a range of 120°—from 360° to 480°. It has been shown that trustworthy results cannot be obtained in experiments in which carbonyl chloride is heated in glass reaction

vessels for long periods. The results obtained in quartz vessels agree fairly well with those of Bodenstein and Plaut.

The values of the logarithms of the constants when plotted against the reciprocals of the absolute temperatures lie on a straight line.

Values calculated for the heat of the reaction show that this changes by an amount less than the uncertainty in Thomsen's values when measured at room temperature and at temperatures between 300° and 500°.

These facts lead to the conclusion that the difference between the sum of the molar heats of carbon monoxide and chlorine and that of carbonyl chloride is constant up to 500°, and that its numerical value is small.

Qualitative evidence was obtained in support of the observations of Christiansen that the decomposition of carbonyl chloride is catalysed by the products of decomposition.

The author wishes to express his thanks to Mr. D. L. Chapman and Mr. H. J. George for the help and criticism which they have given during the course of the work. He is also indebted to the Department of Scientific and Industrial Research for a grant which enabled him to undertake the work.

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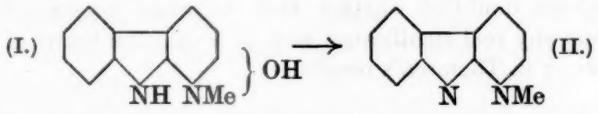
CCCI.—*Polynuclear Heterocyclic Aromatic Types. Part III. Pyrroloquinoline Derivatives.*

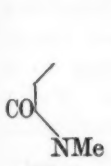
By REGINALD CLIFFORD FAWCETT and ROBERT ROBINSON.

IN Part II of this series (Armit and Robinson, J., 1925, **127**, 1604) several anhydronium bases of the carboline type were described, and 3-carboline methohydroxide (I), for example, was shown to be dehydrated with the formation of the anhydride (II). An

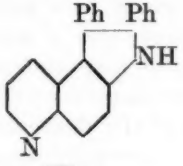


attempt was made to reproduce this phenomenon in the case of a base in which the pyridine and pyrrole rings were separated by a naphthalene nucleus, but without definite result; we have now made similar trials with compounds in which the separation of the heterocyclic nuclei is by a benzene nucleus. A study of the literature showed that the particular combinations of fused

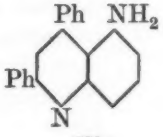
rings which we wished to examine are not contained in known substances, and some difficulty has been experienced in effecting the necessary syntheses. 6-Aminoquinoline and benzoin (compare Japp and Murray, J., 1894, **65**, 889) could be condensed with formation of a *diphenylpyrroloquinoline* (III), but the *methosulphate* of this base, on treatment with aqueous potassium hydroxide, does not appear to yield an anhydro-base. It was thought that less ambiguous results would be obtained if the quinoline ring were



(IIIA.)



(III.)



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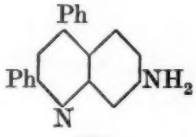
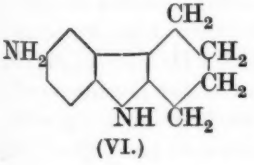


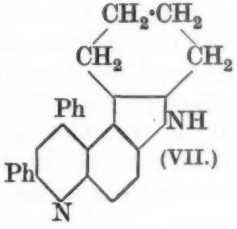
(V.)

phenylated in positions 2 and 4 in order to stabilise the α- and γ-carbinols and thus prevent oxidation to quinolones. The condensation of dibenzoylmethane and *p*-aminoacetanilide could not, however, be effected. With *m*-phenylenediamine the isomeric *aminodiphenylquinolines* (IV, V) were obtained, although in such poor yield that further work along these lines was prohibited.

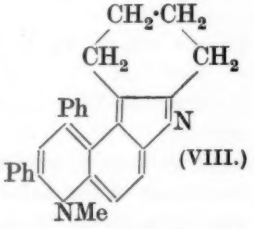
We therefore turned our attention to a scheme in which the quinoline ring is the last to be introduced. 6-Aminotetrahydrocarbazole (VI) (Plant and Edwards, J., 1923, **123**, 2393) and dibenzoylmethane give rise to the intermediate *phenyl tetrahydrocarbazylaminostyryl ketone*, $COPh{\cdot}CH{:}CPh{\cdot}NH{\cdot}C_6H_3\overset{NH}{\diagdown\!\diagup}C_2H_2{:}C_4H_8$, which may be dehydrated by means of phosphoryl chloride with formation of a *diphenyltetrahydroindoloquinoline* (VII). This



(VI.)



(VII.)

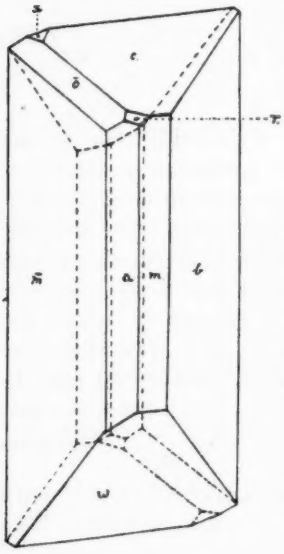


(VIII.)

yellow base gives red salts, and when dissolved in organic solvents it absorbs a molecular proportion of oxygen so as to produce a *dioxy-compound*, $C_{27}H_{22}O_2N_2$. The *substance* derived from the *methosulphate* of (VII) by the action of aqueous potassium hydroxide has, apparently, the composition $C_{28}H_{24}N_2,2H_2O$. In view of its deep green colour and the avidity which it displays for oxygen, it is better regarded as a hydrate of the anhydro-base (VIII) than

of the methohydroxide of (VII) (which should be red, like the methosulphate). Probably the most satisfactory conception of the nature of these intensely-coloured, hydrated anhydro-bases, several of which have now been found to exist, is that which would class them with the pyranhydrones and flavanhydrones as quinhydrones. Thus the substance under discussion would, on this hypothesis, have the composition, $C_{28}H_{24}N_2,C_{28}H_{26}N_2O,3H_2O$. The first component would be the fractional dipolar anhydronium base (compare Part II, *loc. cit.*), whilst the second would be a partly dissociated carbinol-amine, also a fractional dipole, balancing the first and cohering to it through electrostatic attraction. Such a conception of the molecular combination seems to be generally applicable to the quinhydrones.

FIG. 1.



EXPERIMENTAL.

5 : 6-(2′ : 3′-*Diphenylpyrrolo*)(4′ : 5′)-*quinoline* (III).—This base may be obtained from *p*-nitroaniline in an over-all yield of 43%, the yield in the last stage described below being 95%. A mixture of 6-aminoquinoline (7 g.), its hydrochloride (3 g.), and benzoin (15·5 g.) was heated for 4 hours at 150—160°. On cooling, the mass set to a hard cake which was ground with aqueous ammonia, and the yellow powder collected, washed, dried, and crystallised from methyl alcohol and then from ethyl acetate; short, yellow prisms (19 g.), m. p. 167—168° (Found, in material dried at 100°: C, 81·4; H, 5·4; in material dried at 140° in a high vacuum: C, 86·0; H, 5·3. $C_{23}H_{16}N_2,H_2O$ requires C, 81·6; H, 5·3; $C_{23}H_{16}N_2$ requires C, 86·2; H, 5·0%). The molecule of water is tenaciously held and only removed very slowly at 110—120° in a vacuum. Solutions of the substance in most organic solvents are yellow and exhibit a green fluorescence.

A sample of this base was crystallised from ethyl acetate, and the following crystallographic description was kindly supplied by Mr. H. E. Buckley, of the Crystallography Department of this University :

Symmetry : anorthic, pinacoidal. Habit : short prisms, parallel to zone (001). Forms developed : $a(100)$, $b(010)$, $c(001)$, $m(110)$, $\overline{m}(1\bar{1}0)$, $\delta(1\bar{1}1)$, $w(11\bar{1})$, $r(101)$, $x(0\bar{1}3)$.

Table of Observed Angles.

Faces.	Angle.	No. of measurements.	Limits.
(010—$\bar{1}$10)	59° 41′	11	59° 20′—59° 56′
(100—110)	47° 50′	3	47° 45′—47° 57′
(100—1$\bar{1}$0)	33° 7′	5	33° 0′ —33° 13′
(110—010)	39° 28′	2	39° 28′ (each)
(001—010)	74° 51′	8	74° 35′—75° 3′
(001—$\bar{1}$10)	95° 56′	5	95° 46′—96° 6′
(001—1$\bar{1}$1)	42° 0′	7	41° 42′—42° 11′
(1$\bar{1}$1—1$\bar{1}$0)	42° 2′	6	41° 46′—42° 8′
(010—1$\bar{1}$1)	54° 13′	6	54° 5′ —54° 23′
(110—1$\bar{1}$1)	43° 13′	3	43° 4′ —43° 18′
(00$\bar{1}$—11$\bar{1}$)	69° 1′	6	68° 51′—69° 10′
(001—0$\bar{1}$3)	17° 29′	1	17° 29′

Axial angles : $\alpha = 80° 37′$; $\beta = 70° 8′$; $\gamma = 77° 3′$.
$a : b : c = 0{\cdot}601 : 1 : 0{\cdot}530$.

Optics. When the crystal is laid on face $\overline{m}(1\bar{1}0)$, which is usually the largest face, there is an extinction, in parallel polarised light, practically parallel to the edge given by the $c(001)$ face and the prism. From observations in convergent polarised light, it appears that the birefringence is very strong and positive, whilst the dispersion appears to be of the type $\rho > \nu$.

The *hydrogen sulphate* and the *hydrochloride* crystallise from water and from dilute hydrochloric acid respectively in stellar clusters of pale yellow plates. The solution in concentrated sulphuric acid is both colourless and non-fluorescent. The *picrate* crystallises from alcohol in bright yellow needles, m. p. 218° (decomp.).

The Methosulphate.—Pure methyl sulphate (4 g.) in dry benzene (10 c.c.) was added to a solution of diphenylpyrroloquinoline (5 g.) in hot dry benzene (100 c.c.), and the mixture boiled. Bright yellow needles soon appeared and in 10 minutes filled the liquid. The salt was isolated and crystallised from water in yellow needles (5 g.), m. p. 218—219° (Found : S, 7·1. $C_{25}H_{22}O_4N_2S$ requires S, 7·2%). The orange-yellow, alcoholic solution exhibits a faint fluorescence, but the light yellow acetic acid solution has a vivid light green fluorescence. The colourless solution in concentrated sulphuric acid is not fluorescent, but on the addition of water the yellow colour and green fluorescence appear. The solubility in water is approximately : at 25°, 1 part in 70 parts; at 95°, 1 part in 7 parts. Decomposition of this methosulphate with 50% aqueous potash yielded an amorphous red powder.

2-Keto-1-methyl-5 : 6-(2′ : 3′-diphenylpyrrolo)(4′ : 5′)-1 : 2-dihydroquinoline (III, modified as in IIIA).—A cold concentrated aqueous solution of the above methosulphate (4 g.) was added to a 10% sodium hydroxide solution (50 c.c.) containing potassium ferri-

cyanide (5·9 g.), and the mixture was kept for an hour and frequently shaken. The product was isolated by means of ether and then extracted with boiling light petroleum; the solutions on concentration to a small volume deposited a pale yellow powder. The *quinolone* crystallised from ether in pale yellow needles, m. p. 195·5° (Found: C, 78·8; H, 5·2. $C_{24}H_{18}ON_2,H_2O$ requires C, 78·3; H, 5·4%); it is readily soluble in most organic solvents.

5- *and* 7-*Amino*-2 : 4-*diphenylquinoline* (IV, V).—*p*-Aminoacetanilide condenses with dibenzoylmethane to an anil, but ring closure of this could not be effected under a variety of conditions. The action of sulphuric acid on the anil, followed by treatment with aqueous sodium hydroxide gave a *substance*, m. p. 237·5—238·5°, crystallising from alcohol. This appeared to be the sodium salt of a sulphonic acid of the required base. 70% Sulphuric acid and also zinc chloride gave no useful results. We therefore directed our attention to *m*-phenylenediamine derivatives, but here too the experiments met with little success, since the yields of the desired aminodiphenylquinolines were only 5%. A mixture of *m*-phenylenediamine (6 g.) and dibenzoylmethane (12 g.) was heated at 140° for 1 hour; powdered zinc chloride (10 g.) was then introduced, and the temperature maintained at 175—180° for 5 hours. The bases produced were rendered to benzene, and the dried extract on concentration and keeping deposited a mixture of short, thick, prismatic needles and fine, silky needles. These were separated, and after many crystallisations from alcohol and benzene the two forms were obtained pure, their m. p.'s not being altered by further crystallisation; the former variety had m. p. 168·5° (Found: C, 85·0; H, 5·5%), and the latter had m. p. 187° (Found: C, 84·5; H, 5·8. $C_{21}H_{16}N_2$ requires C, 85·1; H, 5·4%); by analogy with other 5- and 7-substituted quinoline derivatives, the substance, m. p. 168·5°, should be the 5-substituted isomeride. The yellow colour of the base, m. p. 187°, is the paler of the two, but in other respects the properties of these substances are closely similar; a mixture had m. p. 142°. The bases may be diazotised, and then couple with β-naphthol to give bright red azo-compounds.

6-*Amino*-1 : 2 : 3 : 4-*tetrahydrocarbazole* (VI).—*p*-Nitrophenylhydrazine (the method of Hodgson and Beard, *J. Soc. Chem. Ind.*, 1926, **45**, 56T, gives almost theoretical yields) was converted into 6-nitrotetrahydrocarbazole, as described by Borsche, Witte, and Bothe (*Annalen*, 1908, **359**, 53) (yield, 80%), but the recorded processes for the reduction of this substance (compare Perkin and Plant, J., 1921, **119**, 1833; Plant and Edwards, *loc. cit.*) gave only 20—40% yields. The use of sodium sulphide as the reducing agent led to still lower results, but a 73% yield was obtained by

means of iron powder and hydrochloric acid in alcoholic solution (compare West, J., 1925, **127**, 494). 6-Nitrotetrahydrocarbazole (20 g.), dissolved in boiling 90% alcohol (70 c.c.) (reflux condenser, mechanical stirrer, and wide, stoppered side-tube) and concentrated hydrochloric acid (1 c.c.), was reduced by the gradual addition of iron powder (24 g.) during 45 minutes and subsequent boiling for 3—4 hours. The mixture was filtered hot and the residue washed with boiling alcohol; the amine (12·5 g.) was isolated from the filtrate by precipitating neutral impurities with concentrated hydrochloric acid (50 c.c.) and separating the hydrochloride by the further addition of hydrochloric acid (100 c.c.). Extraction of the neutral substances by water yielded some more amine hydrochloride, and the final acid mother-liquor was concentrated, basified with ammonia and the crude base crystallised from water.

Phenyl α-Tetrahydrocarbazylamino(6)*-styryl Ketone.*—A mixture of dibenzoylmethane (9·5 g.), 6-aminotetrahydrocarbazole (7·6 g.), and acetic acid (35 c.c.) was refluxed for 1 hour, and the solvent then removed by distillation under diminished pressure. The residue crystallised from alcohol in yellow prisms (8 g.), m. p. 229·5—230° (Found: C, 82·1; H, 6·2. $C_{27}H_{24}ON_2$ requires C, 82·6; H, 6·1%). This substance has very feebly basic properties, and when boiled with hydrochloric acid it first gives a red substance and is then slowly hydrolysed. Its solution in concentrated sulphuric acid is yellow and non-fluorescent, but on keeping the colour fades and a bright violet fluorescence develops; on the addition of water a red salt is precipitated.

2 : 4-*Diphenyl*-5 : 6-(4′ : 5′ : 6′ : 7′-*tetrahydroindolo*)(2′ : 3′)-*quinoline* (VII).—This substance may be obtained from the foregoing ketone in several ways, *e.g.*, (1) by keeping a cold sulphuric acid solution for 24 hours, (2) by heating a sulphuric acid solution to 60—65° for 5 minutes, (3) by passing hydrogen chloride into a solution in acetic acid, and (4) by heating it with half its weight of zinc chloride or phosphoric anhydride. The best procedure is the following: A mixture of the ketone (12·5 g.) and phosphoryl chloride (80 c.c.) was boiled for 1 hour, and the red liquid then gradually added to ice and water with stirring. The dull red solid was collected, washed with water, and triturated with ammonia; the resulting light yellow powder was collected, washed, dried at 105°, and extracted with ether in a Soxhlet apparatus from which air was excluded by means of carbon dioxide; the ethereal solution, on keeping, deposited yellow crystals which were collected and washed in an atmosphere of carbon dioxide, and finally dried in a vacuum desiccator (total yield, 9·5 g., 76%) (Found: C, 86·4; H, 6·1. $C_{27}H_{22}N_2$ requires C, 86·6; H, 5·9%). 2 : 4-*Diphenyl*-

5 : 6-(4′ : 5′ : 6′ : 7′-*tetrahydroindolo*)(2′ : 3′)-*quinoline* crystallises from ether in yellow prisms, m. p. 235°, and dissolves in most organic solvents to yellow solutions exhibiting a greenish-blue fluorescence. Its salts are red and sparingly soluble in water. The red solution in acetic acid gives a pink precipitate on addition of water, whilst the colourless solution in sulphuric acid exhibits a brilliant violet fluorescence. The *picrate*, prepared in alcoholic solution in an atmosphere of carbon dioxide, crystallised in orange-red needles, m. p. 241° (decomp. 243°). The most characteristic property of the base is the ease with which it absorbs oxygen from the air when in solution in organic solvents, especially ether or chloroform; it appears to be relatively stable in the solid state. The product, *dioxydiphenyltetrahydroindoloquinoline*, is readily isolated and crystallises from ether in long, colourless needles which decompose suddenly with bright incandescence at 168°, but without melting (Found: C, 79·4; H, 5·6; N, 6·7. $C_{27}H_{22}O_2N_2$ requires C, 79·8; H, 5·4; N, 6·9%). The dirty green solution in concentrated sulphuric acid slowly develops a most intense green fluorescence, giving the effect of opacity. The incandescence observed on heating suggests that this curious substance is a peroxide.

Metho-derivatives.—A mixture of the base (5 g.), pure methyl sulphate (3·6 g.), and benzene (140 c.c.) was boiled for 2·5 hours, air being displaced from the apparatus by nitrogen. The solvent was removed by distillation, the residual red oil dissolved in dry acetone (about 20 c.c.), and on keeping, red needles separated. These were collected (3·5 g.), and a further quantity (0·6 g.) could be obtained from the mother-liquor by concentration to two-thirds of its volume (further concentration gave uncrystallisable material). The separated *methosulphate* is sparingly soluble in acetone and moderately readily soluble in water. On heating, it decomposes at a high temperature without melting. The colourless solution in concentrated sulphuric acid exhibits a brilliant violet fluorescence. The related *methopicrate* crystallised from acetone in long, slender, meshed, orange-red needles, m. p. 252—254° (decomp.).

The methosulphate (4 g.) was added to benzene (100 c.c.) and 50% aqueous potassium hydroxide (50 c.c.), and the mixture heated for 1½ hours with occasional shaking; air in the apparatus was displaced by nitrogen. The bright red colour in both layers disappeared, the aqueous solution becoming colourless and the benzene layer intense brilliant green. In all the subsequent operations access of air was prevented by nitrogen. The aqueous layer was siphoned off and potassium hydroxide (35 g.) added to

the benzene layer, which was then boiled for 1 hour, filtered, and dried for 12 hours over potassium hydroxide. The solution was filtered, heated, and the base precipitated by the addition of boiling light petroleum (b. p. 60—80°) as a bright green solid, which was collected and dried in a vacuum. At this stage there was for the first time a momentary contact with air, but the desiccator had been previously filled with nitrogen and was quickly evacuated. Weighing was carried out with the utmost dispatch, since absorption of oxygen was obviously indicated during the operation (Found: C, 79·3, 78·8; H, 6·4, 6·3. $C_{28}H_{28}O_2N_2$ requires C, 79·2; H, 6·6%). The dark green powder becomes brown and then black when exposed to air. Treatment with acids gives red salts resembling the metho-salts mentioned above, and the solution in sulphuric acid exhibits violet fluorescence.

The authors desire to thank the Government Grant Committee of the Royal Society for a grant which defrayed a part of the cost of the work, and the Advisory Council of the Department of Scientific and Industrial Research for a grant that enabled one of them to take part in the investigation.

THE UNIVERSITY, MANCHESTER. [*Received, July 11th*, 1927.]

CCCII.—*The Conversion of Palmatine into its Cryptopine Analogue (Cryptopalmatine).*

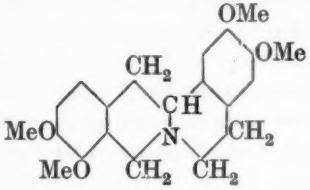
By ROBERT DOWNS HAWORTH, JOSEPH BLAKE KOEPFLI, and WILLIAM HENRY PERKIN, jun.

AN examination of the structural formulæ of the naturally occurring alkaloids of the ten-membered ring type, such as cryptopine and protopine, reveals the relationship between these alkaloids and those of the protoberberine series. Thus the protoberberine alkaloids berberine and coptisine (Kitasato, *Proc. Imp. Acad. Tokyo*, 1926, **2**, 124) are related to the ten-membered ring alkaloids β-homochelidonine and protopine, respectively. These relationships, together with the interconvertibility of the two types, leave little doubt that the further examination of natural products will result in the discovery of new affinities of the same kind. *epi*-Berberine, the protoberberine derivative corresponding to cryptopine, has so far not been isolated from natural sources, whilst the ten-membered ring analogue of palmatine has not been described either as a natural or as a synthetical product. This analogue of palmatine, for which we suggest the name "*cryptopalmatine*" (V), has now been obtained from palmatine by a process similar to that

employed in the synthesis of β-homochelidonine, cryptopine, and protopine (Haworth and Perkin, J., 1926, **129**, 445, 1769).

Tetrahydropalmatine (I) * was treated with methyl iodide and thus converted into the *methiodide* which exists in the usual α- and β-modifications, readily separable by crystallisation from methyl alcohol and then from water. The β-*methochloride*, obtained from the methiodide by the action of silver chloride, is a well-defined,

(I.)



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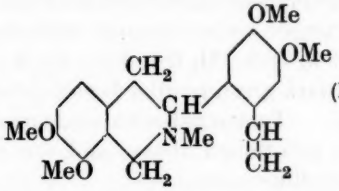


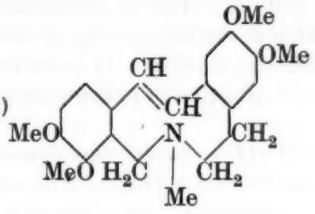
crystalline substance, whereas the corresponding α-*methochloride* has only been isolated as a hygroscopic syrup. When the methiodides or methochlorides are heated with methyl-alcoholic potassium hydroxide, *anhydromethyltetrahydropalmatine B* (II) is obtained as a crystalline substance, m. p. 115—116°, the constitution of which is proved by the facts (i) that it is a stable substance remaining unchanged after digestion with methyl alcohol or chloroform, and (ii) that its sparingly soluble, crystalline *hydrochloride* is not converted into tetrahydropalmatine methochloride by prolonged boiling with dilute hydrochloric acid.

Tetrahydropalmatine methiodide was next converted into the corresponding methohydroxide, by treatment with silver hydroxide in aqueous suspension, and the methohydroxide decomposed by evaporating the solution in a good vacuum, whereby a mixture of *anhydromethyltetrahydropalmatine A* (III) and B (II) was obtained, in which unfortunately the latter modification largely predominated. The former base possesses the properties characteristic of the "A" type, since it is unstable and is converted into tetrahydropalmatine methochloride by warming with dilute hydrochloric acid. Owing to the poor yield of this base, further experiments could only be carried out on a very small scale, and no attempt was made to isolate in a pure condition the amine oxide (IV), which results from the action of perbenzoic acid on the anhydro-base A (III). It was, however, observed that the amine oxide is soluble in water and yields a colourless, sparingly soluble *hydrochloride*. On warming with glacial acetic acid and hydrochloric acid, this amine oxide is readily converted into *cryptopalmatine* (V), a well-defined base which

* We are indebted to Professor Späth for some of the palmatine iodide used in this investigation, but most of the material was prepared by us from berberine by the method of Späth and Quietensky (*Ber.*, 1925, **58**, 2267).

separates from ether in prisms, m. p. 148—150°, and, like cryptopine, gives a characteristic red-violet coloration with sulphuric acid.

(III.)



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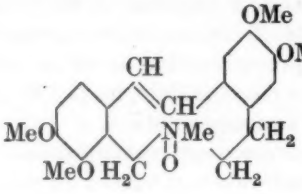

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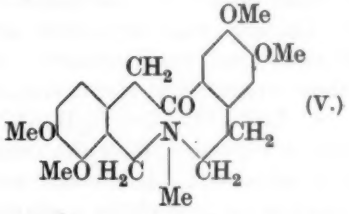

We hope, at a later date, to be able to obtain further quantities of cryptopalmatine, so that it may be possible to make a more complete examination of this interesting base.

Experimental.

Tetrahydropalmatine α- and β-Methiodides.—Tetrahydropalmatine (4 g.), methyl iodide (5 c.c.), and benzene (40 c.c.) were heated on the steam-bath for 4 hours, and the pale yellow methiodide (4·6 g.) was collected, dried, and fractionally crystallised from methyl alcohol (200 c.c.). The first fractions, recrystallised from water, yielded the *β-methiodide* as stout prisms, m. p. 266° (decomp.) * (Found: C, 53·0; H, 5·8. $C_{22}H_{28}O_4NI$ requires C, 53·1; H, 5·6%). This substance is very sparingly soluble in methyl alcohol or water. The last fractions from the crystallisation from methyl alcohol were recrystallised from water, and the *α-methiodide* separated in colourless prisms, m. p. 230°. The crystals contain water of crystallisation, but they lose it at 110° and fall to a powder (Found, in material dried at 110°: C, 53·2; H, 5·9).

Tetrahydropalmatine α- and β-Methochlorides.—The methiodide (*i.e.*, the mixture of the α- and β-forms), suspended in water, was heated with excess of silver chloride on the steam-bath for 3 hours. The filtered solution was concentrated to a small bulk, whereupon the *β-methochloride* separated and was collected. The mother-liquor, on further concentration, yielded the *α-methochloride* as a

* The melting points of the salts given in this and the following papers vary very much with the rate of heating, and must be considered as only approximate.

hygroscopic syrup. The β-methochloride crystallises from water in colourless prisms, m. p. 250° (decomp.) (Found: C, 64·8; H, 7·2. $C_{22}H_{28}O_4NCl$ requires C, 65·1; H, 6·9%). The α-methochloride separates from water as a syrup, which is readily soluble in alcohol and is precipitated as an oil on the addition of ether. It is converted into the α-methiodide, m. p. 230°, by the addition of potassium iodide to the aqueous solution.

Anhydromethyltetrahydropalmatine B (II).—Tetrahydropalmatine methochloride was heated on the steam-bath for 2 hours with excess of 10% methyl-alcoholic potassium hydroxide. The solution was diluted with water, the oily base extracted with ether, and the extract dried, filtered, and concentrated; *anhydromethyltetrahydropalmatine B* then separated in stout, colourless prisms, m. p. 115—116° (Found: C, 71·3; H, 7·5. $C_{22}H_{27}O_4N$ requires C, 71·5; H, 7·3%). This base is very soluble in the usual organic solvents with the exception of petroleum. It is stable towards hot aqueous methyl alcohol or chloroform and yields a sparingly soluble *hydrochloride* which crystallises from water in nodular clusters of needles, m. p. 210° (decomp.); these contain water of crystallisation some of which is lost at 100°, the crystals falling to a powder, but 1 mol. of water is retained after drying at 110° (Found, in material dried at 110°: C, 63·0; H, 7·1. $C_{22}H_{28}O_4NCl,H_2O$ requires C, 62·4; H, 7·1%).

Anhydromethyltetrahydropalmatine A (III).—Tetrahydropalmatine methiodide (3 g.) was digested with a suspension of silver hydroxide until conversion into the methohydroxide was complete. The filtered solution was evaporated and the residue heated for an hour at 100°, both processes being conducted in a vacuum. The syrup which remained was extracted several times with ether, in order to separate the anhydro-bases from any undecomposed methohydroxide, and the ether allowed to evaporate slowly; *anhydromethyltetrahydropalmatine A* gradually separated in needles (0·1 g.), m. p. 131—132° (Found: C, 71·5; H, 7·1. $C_{22}H_{27}O_4N$ requires C, 71·5; H, 7·3%), whilst the modification B (1·5 g.) slowly crystallised from the mother-liquors. Anhydromethyltetrahydropalmatine A is an unstable base which dissolves in cold dilute hydrochloric acid and may be liberated from the solution by sodium hydroxide. After boiling in dilute acid for some time, the base does not separate on the addition of sodium hydroxide, conversion into tetrahydropalmatine methochloride evidently having taken place.

Cryptopalmatine (V).—Anhydromethyltetrahydropalmatine A (0·2 g.) in chloroform (5 c.c.) was gradually added to an ice-cold ethereal solution of perbenzoic acid (0·25 g. in 25 c.c.). The mixture was kept over-night during which it acquired a greenish-yellow tint,

but no crystalline material separated as in the cases previously examined (Haworth and Perkin, *loc. cit.*). When the mixture was shaken with very dilute hydrochloric acid and the extract concentrated in a vacuum, the *hydrochloride* of the amine oxide (IV) separated in colourless prisms, m. p. 198—200° (decomp.) with previous darkening. Owing to scarcity of material the amine oxide was not isolated, but it was observed to be soluble in water because an aqueous solution of the hydrochloride remained clear on the addition of sodium hydroxide.

The hydrochloride (0·1 g.) was dissolved in glacial acetic acid (2 c.c.) and concentrated hydrochloric acid (2 c.c.), boiled for 2 minutes, the brown solution diluted with water, made alkaline with sodium hydroxide, and the amorphous base extracted with chloroform; when the extract was dried and the solvent removed, a brown semi-solid mass remained. This was dissolved in a little alcohol, mixed with a large volume of ether, filtered from amorphous material, the ethereal solution well washed with water, dried over potassium carbonate, filtered, and the solvent allowed to evaporate slowly, whereupon *cryptopalmatine* separated in small, colourless prisms, m. p. 148—150° (Found: C, 68·6; H, 6·8. $C_{22}H_{27}O_5N$ requires C, 68·8; H, 7·0%). A solution of the base in glacial acetic acid developed a reddish-violet coloration on the addition of concentrated sulphuric acid.

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[*Received, August 5th*, 1927.]
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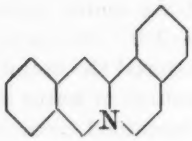
CCCIII.—*Synthetical Experiments in the* iso*Quinoline Group. Part VII. A Synthesis of* 3:11-*Dimethoxyprotoberberinium Salts.*

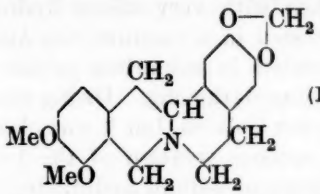
By SATYENDRA NATH CHAKRAVARTI, ROBERT DOWNS HAWORTH, and WILLIAM HENRY PERKIN, jun.

A COMPARISON of the constitutional formulæ of groups of alkaloids brings to light many curious generalities. It is difficult to understand why so many of these substances are built up on a common skeleton and why certain groups, and more particularly methoxy- and methylenedioxy-groups, should play so prominent a part in their structure. Attention has already been directed to the fact (J., 1926, 33) that the alkaloids palmatine, berberine, corydaline, and many others are all derived from the same angular structure (I),

a point clearly illustrated by the formula of tetrahydroberberine (II). It was also pointed out that β-homochelidonine, cryptopine,

(I.)

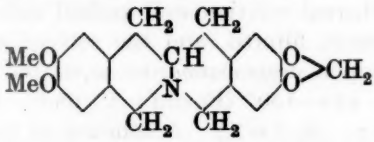




(II.)

and protopine, although not actually derivatives of (I), readily yield quaternary salts which are built up on this skeleton. In order to obtain some light on the reason why the skeleton (I) is so commonly selected by nature, the alkaloid 2 : 3-methylenedioxy-11 : 12-dimethoxy-6 : 15 : 16 : 17-tetrahydroparaberine (IV),* isomeric with tetrahydroberberine, but differing from it in containing the linear structure (III), was synthesised (*loc. cit.*, p. 42).

(III.)



(IV.)

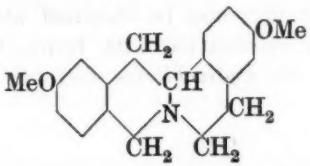
During the course of those experiments, it soon became evident that the various stages in the synthesis did not proceed so smoothly as in the case of the corresponding stages in the synthesis of tetrahydro-ψ-berberine, and furthermore, the properties of the substance (IV) were not nearly so definite and characteristic as those of tetrahydroberberine. In particular, the property of yielding highly coloured quaternary salts on treatment with iodine or other oxidising agents, so strikingly shown by tetrahydroberberine, fails entirely in the case of the paraberine analogue (*loc. cit.*, p. 37). These observations led to the suggestion that the greater ease of formation and more characteristic properties of alkaloids built up on the angular type may have some bearing on the occurrence and preferential selection of this type in nature.

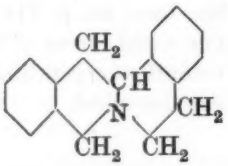
Another remarkable feature, not only of the alkaloids of the berberine group, but also of many others of widely different origin, *e.g.*, narcotine, cryptopine, corycavidine, and glaucine, is the occurrence in the molecule of two catechol nuclei, usually modified by methoxy- or methylenedioxy-groups, although in some cases, *e.g.*, corydine and corytuberine, a hydroxy-group remains free. There can be no doubt that the presence of these methoxy- and methylenedioxy-groups has a profound bearing on the ease of synthesis and

* This alkaloid is actually more directly related to tetrahydro-ψ-*epi*berberine (J., 1924, **125**, 1677).

characteristic properties of these alkaloids, and there are also indications, to which reference has been made (this vol., p. 2262), that these groups also greatly influence the possibility of converting the alkaloids into derivatives of the ten-membered ring type (compare J., 1926, 446), and consequently into alkaloids of the β-homochelidonine group. In view of these considerations it seemed to be of interest to attempt to prepare alkaloids which, although built up on the angular skeleton (I), do not contain a catechol nucleus, and to compare the ease of synthesis and characteristic properties of such substances with these features in the case of the alkaloids of the palmatine–berberine type.

The present communication deals with the synthesis of 3 : 11-*dimethoxytetrahydroprotoberberine* (V) * containing two methoxy-groups, and in the succeeding investigation we describe the synthesis of tetrahydroprotoberberine itself (VI), which contains no methoxy-groups and to which special interest attaches because it is the parent of the whole palmatine–berberine group of alkaloids.

(V.) 

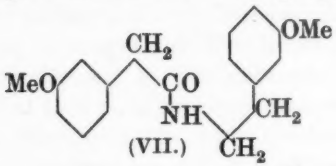
 (VI.)

The synthesis of 3 : 11-dimethoxyprotoberberine and its derivatives was conducted in the following manner. β-*m*-Methoxyphenylethylamine, prepared by a slight modification of the method of Helfer (*Helv. Chim. Acta*, 1924, **7**, 945), was condensed with *m*-methoxyphenylacetic acid, prepared by a method similar to that employed by Pschorr (*Annalen*, 1912, **391**, 41), and the m-*methoxyphenylaceto*-β-m-*methoxyphenylethylamide* (VII) so obtained was converted, in a yield of 80%, into a syrupy base of which the *picrate* is crystalline. This base, which is probably 6-*methoxy*-1-(3′-*methoxybenzyl*)-3 : 4-*dihydroisoquinoline* (VIII), oxidises rapidly on exposure to air and is readily reduced by zinc and sulphuric acid to 6-*methoxy*-1-(3′-*methoxybenzyl*)-1 : 2 : 3 : 4-*tetrahydroisoquinoline* (IX), an oily base yielding a crystalline *sulphate* and *picrate*. Ring-closure of the *formyl* derivative was effected in the usual manner with phosphorus oxychloride, giving a 66% yield of a yellow crystalline base, m. p. 130°, which is doubtless 3 : 11-*dimethoxydihydroprotoberberine* (X).

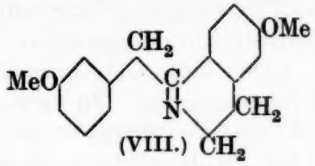
Although we have no direct evidence that the two ring-closures, *i.e.*, the conversion of (VII) into (VIII) and (IX) into (X), have taken place in the para-positions to the methoxy-groups, there can be little doubt that this is the case, since, judging from analogy,

* The nomenclature is discussed in J., 1925, **127**, 1462.

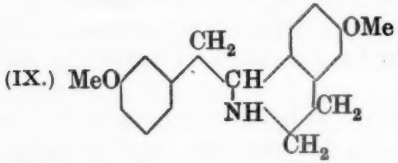
ring-closure in the ortho-positions is most unlikely. Synthetical experiments which are in progress will, we hope, decide this point.



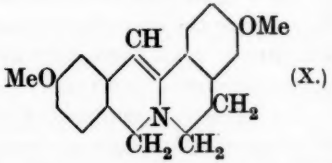
(VII.)



(VIII.)

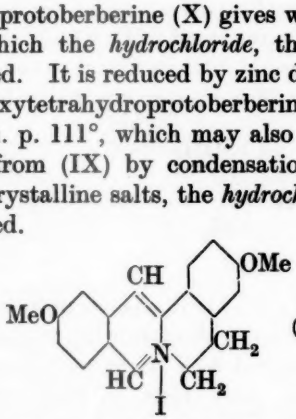


(IX.)



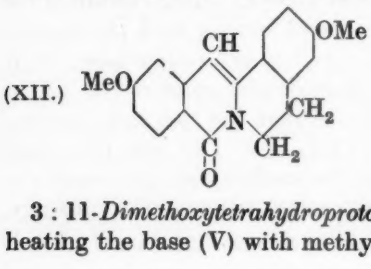
(X.)

Dimethoxydihydroprotoberberine (X) gives well-characterised, pale yellow salts of which the *hydrochloride*, the *hydriodide*, and the *picrate* are described. It is reduced by zinc dust and sulphuric acid to 3 : 11-dimethoxytetrahydroprotoberberine (V), a colourless crystalline base, m. p. 111°, which may also be obtained, although in smaller yield, from (IX) by condensation with formaldehyde. Of the colourless crystalline salts, the *hydrochloride*, *hydriodide*, and *picrate* are described.

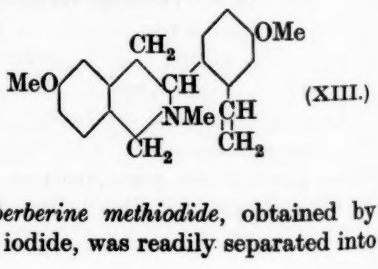


(XI.)

When 3 : 11-dimethoxytetrahydroprotoberberine (V) is oxidised with iodine in alcoholic solution, it yields 3 : 11-*dimethoxyprotoberberinium iodide* (XI), a yellow quaternary salt from which the corresponding yellow *chloride* was prepared. The iodide (XI) is decomposed in the usual manner by potassium hydroxide giving 3 : 11-*dimethoxyoxyprotoberberine* (XII) and dimethoxydihydroprotoberberine (X), which are readily separated, in that the former is insoluble and the latter soluble in dilute mineral acids.



(XII.)



(XIII.)

3 : 11-*Dimethoxytetrahydroprotoberberine methiodide*, obtained by heating the base (V) with methyl iodide, was readily separated into

α- and β-forms by crystallisation from water (compare Pyman, J., 1913, **103**, 825; Haworth and Perkin, J., 1926, 1772), and these were converted into the corresponding *methochlorides*, of which the β-form is crystalline, whereas the α-modification is a syrup. The methiodide was next converted into *anhydromethyl*-3 : 11-*dimethoxytetrahydroprotoberberine B* (XIII) by the action of alcoholic potassium hydroxide, and the interesting observation was made that this is the only base which is obtained when the methiodide is converted by silver hydroxide into the corresponding methohydroxide and the aqueous solution is evaporated in a good vacuum. The structure assigned to this base is confirmed by its stability towards aqueous methyl alcohol and chloroform, and by its yielding a stable and sparingly soluble *hydrochloride*. It is clear from these experiments that the presence of two methoxy-groups attached to the annular skeleton of tetrahydroberberine as in (V) does not allow the formation of the ten-membered ring, at all events under the usual conditions.

The other points of general interest which emerge from this investigation are (i) that the synthetical experiments described proceed almost as readily, if perhaps not quite so smoothly, when only two methoxy-groups are present as they do in the case of the corresponding syntheses in the berberine series, and (ii) that the deep yellow colour of the salts of berberine and allied alkaloids becomes much less intense when only two methoxy-groups are present in the molecule.

EXPERIMENTAL.

m-Methoxybenzaldehyde is obtained in a yield of 80% by the following method : *m*-Hydroxybenzaldehyde (250 g.), methyl alcohol (750 c.c.), and sodium hydroxide (85 g.), dissolved in the minimum of water, are heated on the steam-bath, and freshly distilled methyl sulphate (290 g.) is added sufficiently rapidly to maintain brisk ebullition; a further quantity of methyl sulphate (200 g.) is then added, the mixture being kept alkaline by the addition of 50% sodium hydroxide. The product is kept for ½ hour, the methyl alcohol removed by distillation, and the residue diluted with water and extracted with ether. The extract is dried with sodium sulphate, the ether removed, and the *m*-methoxybenzaldehyde distilled under reduced pressure. *m*-Methoxycinnamic acid was prepared by heating *m*-methoxybenzaldehyde (100 g.), malonic acid (160 g.), and piperidine (5 c.c.) in pyridine (250 c.c.) solution for 1½ hours on the steam-bath, and then boiling for 15 minutes on the sand-bath. The product, on being poured into excess of dilute hydrochloric acid, gave an almost quantitative yield of *m*-methoxycinnamic acid, m. p. 117°. This acid was reduced with sodium amalgam to β-*m*-methoxyphenylpropionic acid in the manner described by Helfer (*loc. cit.*).

m-Methoxyphenylacetic acid was prepared by the method of Pschorr (*loc. cit.*), but a different procedure was adopted in the separation of the products of the hydrolysis of the az-lactone. After hydrolysing the latter with sodium hydroxide, the solution was saturated with sulphur dioxide, the benzoic acid collected, the filtrate acidified and boiled, and the m-*methoxyphenylpyruvic acid* collected and recrystallised from glacial acetic acid, separating in small crystals, m. p. 150° (Found: C, 61·6; H, 5·1. $C_{10}H_{10}O_4$ requires C, 61·8; H, 5·1%). This acid is readily soluble in hot alcohol but rather sparingly soluble in cold acetic acid or toluene. It was oxidised in cold alkaline solution with hydrogen peroxide, and *m*-methoxyphenylacetic acid, m. p. 68°, was obtained in good yield on acidifying the alkaline solution.

m-*Methoxyphenylacet*-β-m-*methoxyphenylethylamide* (VII).—(i) Equivalent quantities of β-*m*-methoxyphenylethylamine (Helfer, *loc. cit.*) and *m*-methoxyphenylacetic acid were heated at 180° for 3 hours. Alternatively, (ii) *m*-methoxyphenylacetic acid (6 g.), dissolved in a little chloroform, was gently boiled for ½ hour with thionyl chloride (3·5 g.); the chloroform was removed and the residual yellow oil added to an emulsion of β-*m*-methoxyphenylethylamine (5 g.) in potassium hydroxide (40 c.c. of 10%), the mixture being well shaken during the addition. By either method, the *amide* was obtained as an oil which did not crystallise in contact with the usual solvents.

6-*Methoxy*-1-(3′-*methoxybenzyl*)-3 : 4-*dihydroisoquinoline* (VIII).—The amide just described (20 g.) was heated with phosphorus oxychloride (50 c.c.) for 2 hours on the steam-bath and then kept over-night. The mixture was decomposed and extracted with hot water (charcoal), filtered from tar, the filtrate made alkaline with sodium hydroxide, and extracted several times with benzene (A). Some of the benzene extract was dried over potassium carbonate, the solvent removed, and the oily base dissolved in alcohol and mixed with an alcoholic solution of picric acid. The yellow *picrate* of (VIII) which separated is sparingly soluble in alcohol and readily soluble in hot glacial acetic acid, from which it separates in small needles, m. p. 155° (Found: C, 56·3; H, 4·6. $C_{24}H_{22}O_9N_4$ requires C, 56·5; H, 4·3%).

6-*Methoxy*-1-(3′-*methoxybenzyl*)-1 : 2 : 3 : 4-*tetrahydroisoquinoline* (IX).—This was obtained by extracting the benzene extract (A) with dilute sulphuric acid, and reducing the acid solution with zinc dust. The solution was made alkaline with ammonia, the tetrahydro-base extracted with chloroform, dried over potassium carbonate, and the solvent removed, leaving the base as an oil. The *hydrochloride*, obtained by dissolving the oil in hot dilute hydro-

chloric acid, and cooling, separated in needles, m. p. 192° (decomp.) (Found : C, 67·9; H, 6·9. $C_{18}H_{22}O_2NCl$ requires C, 67·6; H, 6·9%). The *sulphate* is readily soluble in hot water and crystallises in rhombs. The *picrate*, prepared in alcoholic solution, is sparingly soluble in hot alcohol, and separates from glacial acetic acid as a crystalline powder, m. p. 148° (Found : C, 56·6; H, 4·6. $C_{24}H_{24}O_9N_4$ requires C, 56·3; H, 4·8%).

3 : 11-*Dimethoxydihydroprotoberberine* (X).—The N-*formyl* derivative of (IX) was prepared by adding a slight excess of formic acid to a dry benzene solution of the base; the benzene was removed, and the residue heated in an oil-bath at 200° for 2 hours. The whole (13 g.) was dissolved in dry toluene (50 c.c.), phosphorus oxychloride (30 c.c.) added, and the mixture boiled for 1½ hours. The product was diluted with petroleum ether, the dark brown oil which separated was dissolved in alcohol, made alkaline with sodium hydroxide, and diluted with water; when the sides of the vessel were scratched vigorously, the *base* (X) separated as a yellow powder (8 g.), which crystallised from alcohol or benzene in shining, yellow, rhombic prisms, m. p. 130° (Found : C, 78·0; H, 6·6. $C_{19}H_{19}O_2N$ requires C, 77·8; H, 6·5%). This base is sparingly soluble in alcohol, more soluble in benzene, and readily soluble in chloroform. It is a strong base yielding pale yellow, crystalline salts with mineral acids. The solution in concentrated sulphuric acid is yellowish-brown and becomes deep red on the addition of a crystal of potassium nitrate. The *hydrochloride* is rather sparingly soluble in water or dilute hydrochloric acid, and crystallises from the former in silky needles containing $4H_2O$ which is lost at 105° (Found : loss at 105°, 17·0. Calc. for $4H_2O$: 17·9. Found in material dried at 105° : C, 68·7; H, 6·1. $C_{19}H_{20}O_2NCl$ requires C, 69·2; H, 6·1%). The *hydriodide*, obtained by adding sodium iodide to the aqueous solution of the hydrochloride, is a yellow, crystalline powder, very sparingly soluble in boiling water (Found : C, 54·6; H, 4·8. $C_{19}H_{20}O_2NI$ requires C, 54·2; H, 4·8%). The *picrate*, prepared in alcoholic solution, is very sparingly soluble in alcohol, and separates from glacial acetic acid as a bright yellow, crystalline powder, m. p. 232° (Found : C, 57·4; H, 4·1. $C_{25}H_{22}O_9N_4$ requires C, 57·5; H, 4·2%).

3 : 11-*Dimethoxytetrahydroprotoberberine* (V).—This substance was obtained in two ways. (i) Dimethoxydihydroprotoberberine (X) was reduced by zinc dust and dilute sulphuric acid until the solution became colourless; the product was filtered, the filtrate made alkaline with ammonia, the base extracted with chloroform, dried over potassium carbonate, the solvent removed, and the residue dissolved in dilute hydrochloric acid, from which the *hydrochloride* of the base separated on cooling. This was collected, dissolved in

water, decomposed with concentrated ammonia, and the almost colourless 3 : 11-*dimethoxytetrahydroprotoberberine* crystallised from alcohol or dry benzene. (ii) The tetrahydro-base (IX; p. 2270) was dissolved in methyl alcohol, mixed with sodium bicarbonate and a slight excess of 40% formaldehyde, and the mixture warmed for a few minutes on the steam-bath; on the addition of water and some salt, a gum separated, which was thoroughly washed with cold water and heated with concentrated hydrochloric acid on the steam-bath for a few minutes; the gummy hydrochloride was redissolved in water, decomposed with ammonia, the base extracted with chloroform, and the solvent removed. The residual syrup was rubbed with ether, which removed unchanged tetrahydro-base, and the sparingly soluble residue of dimethoxytetrahydroprotoberberine was crystallised from alcohol or benzene. The yield was small, however, and various modifications of this method failed to effect much improvement.

3 : 11-Dimethoxytetrahydroprotoberberine separates from alcohol or dry benzene in jagged prisms, m. p. 111° (Found: C, 77·6; H, 7·1. $C_{19}H_{21}O_2N$ requires C, 77·3; H, 7·1%), readily soluble in chloroform, or in methyl or ethyl alcohol; the base and its salts are rather more soluble than dimethoxydihydroprotoberberine and its salts. The hydrochloride is readily soluble in hot water, from which it separates in characteristic, colourless rosettes, m. p. 199° (Found: C, 68·8; H, 6·7. $C_{19}H_{22}O_2NCl$ requires C, 68·8; H, 6·6%). The *hydriodide*, obtained by adding sodium iodide to the aqueous solution of the hydrochloride, is moderately soluble in boiling water and separates as a crystalline powder with a very slight yellow tinge, m. p. 205° (Found: C, 54·4; H, 5·2. $C_{19}H_{22}O_2NI$ requires C, 53·9; H, 5·2%). The *picrate*, prepared in alcoholic solution, separates from glacial acetic acid or alcohol in bright yellow needles, m. p. 139—140° (decomp.) (Found: C, 57·5; H, 4·9. $C_{25}H_{24}O_9N_4$ requires C, 57·3; H, 4·6%).

The 3 : 11-*Dimethoxyprotoberberinium Salts*.—Dimethoxytetrahydroprotoberberine (V), dissolved in the minimum of boiling alcohol, was mixed with anhydrous sodium acetate, and an alcoholic solution of iodine slowly added until a permanent coloration remained. The dark brown granular *periodide* was collected, washed with water, suspended in hot water, and decomposed by adding aqueous sulphurous acid. The pale yellow *iodide* (XI) separated from water, in which it is very sparingly soluble, in pale yellow needles, m. p. 242° (Found: C, 54·2; H, 4·4. $C_{19}H_{18}O_2NI$ requires C, 54·4; H, 4·3%). The *chloride* is readily obtained by digesting an aqueous suspension of the iodide with excess of silver chloride for 2 hours on the steam-bath; after filtering, concentrating, and adding hydrochloric acid,

the mass of pale yellow needles of the chloride is recrystallised from dilute hydrochloric acid and left on porous porcelain exposed to air for 2 days, m. p. 200° (decomp.). The salt contains $3H_2O$ which is lost at 105° (Found: loss at 105°, 13·5. Calc. for $3H_2O$: 14·1. Found in material dried at 105°: C, 69·3; H, 5·8. $C_{19}H_{18}O_2NCl$ requires C, 69·6; H, 5·5%). The *picrate* was obtained, by adding aqueous picric acid to the hot aqueous solution of the chloride, as yellow flocks almost insoluble in alcohol and sparingly soluble in glacial acetic acid, from which it separates as a feathery mass of long, yellow needles, m. p. 238° (Found: C, 55·5; H, 3·9. $C_{25}H_{22}O_{10}N_4$ requires C, 55·8; H, 4·1%).

3 : 11-*Dimethoxyoxyprotoberberine* (XII).—A boiling aqueous solution of 3 : 11-dimethoxyprotoberberinium chloride (2 g.) was added to a hot solution of potassium hydroxide (8 g.) in water (32 c.c.), and the whole heated on the steam-bath for 2 hours. The yellow mass which separated was collected and thoroughly extracted with dilute hydrochloric acid (A); the residue was dissolved in hot glacial acetic acid, mixed with an equal volume of boiling water, and allowed to stand, the oxy-derivative (XII) then separating as a mass of colourless needles, m. p. 143° (Found: C, 74·1; H, 5·7. $C_{19}H_{17}O_3N$ requires C, 74·3; H, 5·5%). 3 : 11-*Dimethoxyoxyprotoberberine* is sparingly soluble in the usual solvents, except glacial acetic acid, and insoluble in dilute mineral acids. It dissolves in concentrated sulphuric acid to a yellow solution which changes to brown on the addition of a crystal of potassium nitrate.

The hydrochloric acid extracts (A) gradually deposited a mass of pale yellow needles, which were collected, dissolved in water, and precipitated with ammonia. The precipitate was washed and recrystallised from alcohol; the resulting yellow rhombic prisms, m. p. 130°, proved to be identical with the 3 : 11-dimethoxydihydroprotoberberine (X) described on p. 2271.

3 : 11-*Dimethoxytetrahydroprotoberberine Methiodide*.—The base (V; 10 g.) and methyl iodide (15 c.c.) were boiled for 15 minutes, the excess of methyl iodide was removed, and the residue dissolved in boiling water (300 c.c.) and cooled; the β-*methiodide* separated and was crystallised from water as colourless prisms, m. p. 245° (decomp.) (Found: C, 54·9; H, 5·7. $C_{20}H_{24}O_2NI$ requires C, 54·9; H, 5·5%). The α-*methiodide*, obtained by concentrating the mother-liquors, separated from water in colourless nodules, m. p. 224° (Found: C, 55·2; H, 5·6). The methochlorides were obtained by digesting an aqueous suspension of the mixed methiodides with silver chloride. The filtered solution was evaporated to dryness, the pale yellow syrup dissolved in alcohol, and ether slowly added; the β-*methochloride* then separated in colourless needles, m. p. 245° (decomp.)

(Found: C, 69·2; H, 7·1. $C_{20}H_{24}O_2NCl$ requires C, 69·4; H, 6·9%). The *α-methochloride* was precipitated as a syrup by the addition of more ether to the alcohol–ether mother-liquor of the β-methochloride. It was not obtained in a crystalline state, but the addition of sodium iodide to its aqueous solution precipitated the α-methiodide, m. p. 224°.

Anhydromethyl-3 : 11-*dimethoxytetrahydroprotoberberine* (XIII).—(i) The mixed methochlorides (1 g.) were boiled with 25% methyl-alcoholic potassium hydroxide (6 c.c.) for 2 hours, the mixture was diluted with water, the oily base extracted with ether, and the solvent removed, leaving the crude base as a colourless oil which did not solidify; it was soluble in the usual organic solvents and yielded the sparingly soluble *hydrochloride* (see below) when it was stirred with dilute hydrochloric acid. (ii) An aqueous solution of the mixed methiodides or methochlorides was decomposed with silver hydroxide, filtered, the filtrate concentrated in a good vacuum, and the residue extracted with benzene. This left a small amount of material which was dissolved in water and concentrated, giving crystals of 3 : 11-*dimethoxytetrahydroprotoberberine methocarbonate*, m. p. 216°, which dissolved with effervescence in dilute hydrochloric acid (Found: C, 67·9; H, 6·9. $C_{21}H_{25}O_5N$ requires C, 67·9; H, 6·7%). The benzene extract, on concentration, yielded an oil which gave a sparingly soluble hydrochloride and was identical with the oil obtained by method (i); all its properties showed that it was an anhydro-base of the "B" type. *Anhydro*-3 : 11-*dimethoxytetrahydroprotoberberine B* is an oil which decolorises a solution of bromine in chloroform and also an acid solution of permanganate. It is recovered after boiling for several hours with aqueous alcohol or chloroform. The sparingly soluble hydrochloride crystallises from water in small needles, m. p. 236° (decomp.), and is recovered unchanged after boiling with dilute hydrochloric acid for 6 hours (Found: C, 69·2; H, 6·9. $C_{20}H_{24}O_2NCl$ requires C, 69·4; H, 6·9%). When the base (XIII) was mixed with perbenzoic acid, no crystalline material separated. The mixture was extracted with dilute hydrochloric acid, the acid extract evaporated in a vacuum, and the resulting gum warmed with glacial acetic acid and concentrated hydrochloric acid. The reddish solution obtained yielded an amorphous, dark slime on the addition of ammonia, but no crystalline substance could be isolated from it.

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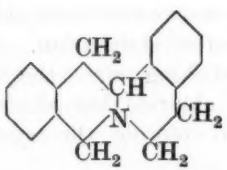
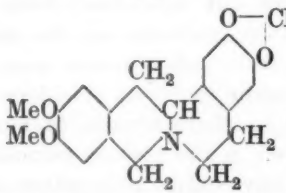
CCCIV.—*Synthetical Experiments in the* iso*Quinoline Group. Part VIII. A Synthesis of Protoberberinium Salts.*

By SATYENDRA NATH CHAKRAVARTI, ROBERT DOWNS HAWORTH, and WILLIAM HENRY PERKIN, jun.

IT is pointed out (preceding paper) that the parent substance of the alkaloids of the palmatine–berberine series is protoberberine, the synthesis of which is now described. It was thought probable that the methods which had proved so successful in the syntheses of ψ-berberine and other similar cases might fail in the present case because the absence of the methylenedioxy- or methoxy-groups might inhibit one or other of the necessary ring-closures. These anticipations were, in fact, largely realised, for although the synthesis was ultimately successful, the yields obtained, especially in the case of the second ring-closure, were so poor that the accumulation of sufficient material for the study of protoberberine was a very tedious process. Clearly, then, the presence of the catechol nuclei is an important factor in facilitating the building up of these alkaloids, and this fact is in harmony with the presence of these nuclei in so many of the naturally occurring alkaloids of this and similar groups.

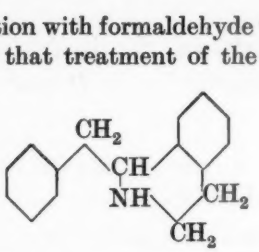
As in previous cases, the first object was the synthesis of *tetrahydroprotoberberine* (I), and the methods employed were similar to those which had been successful in the synthesis of tetrahydro-ψ-berberine (II) and allied substances. Phenylacet-β-phenylethylamide, prepared from phenylacetic acid and β-phenylethylamine,

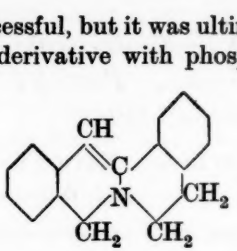
(I.) 

 (II.)

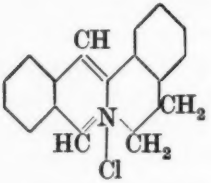
was converted into 1-benzyl-3 : 4-dihydro*iso*quinoline by the action of phosphorus pentoxide (compare Decker and Kropp, *Ber.*, 1909, **42**, 2075; Pictet and Kay, *ibid.*, p. 1976; Forsyth, Kelly, and Pyman, J., 1925, **127**, 1663). On reduction with dilute sulphuric acid and zinc, the dihydro-base yielded 1-benzyl-1 : 2 : 3 : 4-tetrahydro*iso*quinoline (III; compare Forsyth, Kelly, and Pyman, *loc. cit.*, p. 1664), an oily base which gives a crystalline hydriodide and *sulphate*. The conversion of this substance into tetrahydroprotoberberine (I) presented considerable difficulty. The usual con-

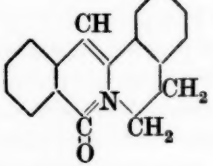
densation with formaldehyde was unsuccessful, but it was ultimately found that treatment of the N-*formyl* derivative with phosphorus

(III.) 

 (IV.)

oxychloride under strictly defined conditions (see p. 2278) yielded small quantities of *dihydroprotoberberine* (IV), the yield under the most favourable conditions not exceeding 10%. (The substitution of phosphorus pentoxide for the oxychloride did not effect any improvement.) The base (IV) was not isolated as such, but was immediately reduced by zinc dust and hydrochloric acid to tetrahydroprotoberberine (I), m. p. 85°, which crystallises well and yields a crystalline *hydrochloride* and *picrate*. When the tetrahydro-base is oxidised in alcoholic solution by iodine, it is converted into *protoberberinium iodide*, which is much less highly coloured than berberinium iodide, crystallises in yellow needles, and is converted by silver chloride into the *chloride* (V). It is interesting

(V.) 

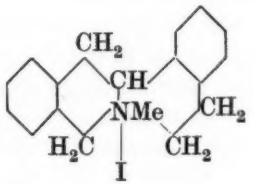
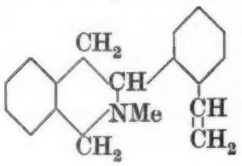
 (VI.)

that this salt crystallises from water with $4H_2O$, thus resembling berberinium chloride and the other analogously constituted chlorides of this series, all of which contain water of crystallisation. In this case, again, the loss of colour is very striking, since the intense yellow so characteristic of berberinium chloride has almost disappeared in the case of protoberberinium chloride, the crystals of which have only a pale yellow tinge.

Protoberberinium chloride is decomposed by potassium hydroxide in the usual manner and yields *oxyprotoberberine* (VI), m. p. 102°, but the dihydroprotoberberine which is evidently produced at the same time could not be isolated in a pure state owing to the small amount of material at our disposal. Attention may be directed to the unexpectedly large effect which the elimination of methoxy- and methylenedioxy-groups has in producing low melting points in the derivatives of protoberberine: thus tetrahydroprotoberberine has m. p. 85°, whereas tetrahydroberberine melts at 170° and

tetrahydropalmatine at 147°; oxyprotoberberine has m. p. 102°, whereas oxyberberine melts at 200° and oxypalmatine at 183°.

Tetrahydroprotoberberine methiodide (VII), prepared by heating the base with excess of methyl iodide, was readily separable into α- and β-forms. When treated with alcoholic potassium hydroxide, the methiodide was converted into *anhydromethyltetrahydroprotoberberine* (VIII), a syrupy base which yields a sparingly soluble *hydrochloride*. The same anhydro-base was obtained when the

(VII.)  (VIII.) 

methiodide was digested with silver hydroxide and the solution evaporated in a good vacuum. No trace of the isomeric base containing a ten-membered ring could be isolated, and the constitution (VIII) is assigned to anhydromethyltetrahydroprotoberberine because the base is stable towards methyl alcohol and chloroform, and the sparingly soluble hydrochloride is also stable towards boiling dilute hydrochloric acid—conditions under which the ten-membered isomeride would be converted into a quaternary chloride. It would appear, therefore, that, in the absence of methoxy- or methylenedioxy-groups, there is no tendency towards the formation of the ten-membered anhydro-base.

Experimental.

1-*Benzyl*-1 : 2 : 3 : 4-*tetrahydro*isoquinoline (III).—To a boiling solution in xylene (100 c.c.) of phenylacet-β-phenylethylamide (20 g.), obtained by heating molecular proportions of phenylacetic acid and β-phenylethylamine at 180° (Decker and Kropp, *loc. cit.*), phosphorus pentoxide (40 g.) was added, and the boiling continued for ½ hour; the mixture was poured into water, the toluene layer removed, and the aqueous layer made strongly alkaline with sodium hydroxide. The 1-benzyl-3 : 4-dihydro*iso*quinoline which separated as an oil (Pictet and Kay, *loc. cit.*) was rapidly extracted with benzene and thence with dilute sulphuric acid; the acid extract gradually deposited the *sulphate* in regular cubes, m. p. 216° (Found : C, 60·4; H, 5·4. $C_{16}H_{15}N,H_2SO_4$ requires C, 60·2; H, 5·3%). The sulphuric acid solution of the sulphate was heated with excess of zinc dust for 1½ hours, reduction then being complete. The hot solution was filtered, decomposed with ammonia, the oily base

extracted with chloroform, the extract dried over potassium carbonate, the solvent removed, and the residual oil dissolved in hot dilute sulphuric acid. The *1-benzyl-1 : 2 : 3 : 4-tetrahydroisoquinoline sulphate*, which gradually formed, crystallised from water with $5H_2O$, of which $4H_2O$ were lost at 100°, m. p. 191° (decomp.) [Found: loss at 100°, 11·2. $(C_{16}H_{17}N)_2,H_2SO_4,5H_2O$ requires $4H_2O$, 11·2. Found in material dried at 100°: C, 67·8; H, 6·7. $(C_{16}H_{17}N)_2,H_2SO_4,H_2O$ requires C, 68·3; H, 6·8%]. This sulphate is less soluble in dilute sulphuric acid than in water.

Tetrahydroprotoberberine (I).—This base could not be obtained by treating the foregoing base with formaldehyde in the usual manner. A variety of conditions were examined and, although small quantities of crystalline hydrochlorides were sometimes formed, they always gave rise to gummy bases on decomposition with alkali. Ultimately the following method was found to give the desired result although the yield was not more than 10%. 1-Benzyl-1 : 2 : 3 : 4-tetrahydro*iso*quinoline (24 g.) and anhydrous formic acid (5 g.) were heated in an oil bath at 200—205° until effervescence had ceased (3 hours). The product was dissolved in toluene and boiled with phosphorus oxychloride (48 c.c.) for 1½ hours; light petroleum was then added, the clear liquid decanted from the dark-coloured gum, the latter extracted with dilute hydrochloric acid (charcoal), and the solution of dihydroprotoberberine hydrochloride reduced by heating with excess of zinc dust for 2 hours, during which the yellow solution became colourless. The hot liquid was filtered, the filtrate decomposed with ammonia, the base extracted with chloroform, dried over potassium carbonate, the chloroform removed, and the residue dissolved in hot dilute hydrochloric acid, from which *tetrahydroprotoberberine hydrochloride* gradually separated. This was collected, recrystallised from water (charcoal), the purified salt dissolved in water, decomposed with ammonia, the base extracted with ether, dried over potassium carbonate, filtered, and the ether allowed to evaporate slowly, whereupon *tetrahydroprotoberberine* crystallised in clusters of colourless needles, m. p. 85° (Found: C, 87·2; H, 7·3. $C_{17}H_{17}N$ requires C, 86·8; H, 7·2%); it dissolves readily in the usual organic solvents, with the exception of petroleum, and crystallises well from either ether or methyl alcohol. It is a strong base dissolving in dilute acids and giving well-characterised salts. Its solution in concentrated sulphuric acid is colourless even after the addition of a crystal of potassium nitrate. This reaction distinguishes tetrahydroprotoberberine from other alkaloids of this series, for the sulphuric acid solutions of all those containing methoxy- or methylenedioxy-groups develop coloration under these conditions. The colours are probably

due to nitration occurring in the nuclei activated by these substituent groups.

Tetrahydroprotoberberine hydrochloride is readily soluble in water, from which it separates in slender needles, m. p. 232° (Found: C, 75·4; H, 6·8. $C_{17}H_{18}NCl$ requires C, 75·1; H, 6·6%), and very sparingly soluble in dilute hydrochloric acid. The still more sparingly soluble, crystalline *hydriodide* separates when a solution of sodium iodide is added to the aqueous solution of the hydrochloride. The *picrate* crystallises in small yellow needles, m. p. 151°, when an alcoholic solution of the base is mixed with picric acid; it is soluble in glacial acetic acid or hot alcohol, sparingly soluble in cold alcohol, and almost insoluble in water (Found: C, 59·0; H, 4·6. $C_{23}H_{20}O_7N_4$ requires C, 59·5; H, 4·3%).

The Protoberberinium Salts (as V).—Tetrahydroprotoberberine, dissolved in the minimum of boiling alcohol, was mixed with anhydrous sodium acetate, and an alcoholic solution of iodine added until a permanent colour remained. The dark brown, granular precipitate of the *periodide* was collected, washed well with water, suspended in water, decomposed with sulphur dioxide, and the resulting yellow *iodide* recrystallised from boiling water; fine yellow needles, m. p. 232° (decomp.) (Found: C, 56·2; H, 4·1. $C_{17}H_{14}NI$ requires C, 56·2; H, 3·9%). The *chloride* was readily obtained when an aqueous suspension of the iodide was digested with excess of silver chloride for 2 hours on the steam-bath. After filtering, concentrating, and adding hydrochloric acid, the chloride separated as a mass of needles having only a slight yellow tinge; it was recrystallised from water and left on porous porcelain exposed to the air for 2 days. It then had the composition $C_{17}H_{14}NCl,4H_2O$, and after heating at 100° it still retained $\frac{1}{2}H_2O$ (Found: loss at 100°, 18·3. $C_{17}H_{14}NCl,4H_2O$ requires $3\frac{1}{2}H_2O$, 18·5. Found in material dried at 100°: C, 74·2; H, 5·5. $C_{17}H_{14}NCl,\frac{1}{2}H_2O$ requires C, 73·8; H, 5·4%). *Protoberberinium picrate* was obtained as yellow flocks on adding aqueous picric acid to a hot aqueous solution of the chloride; it crystallised from glacial acetic acid, in which it is sparingly soluble, in fine, yellow needles, m. p. 192—193°.

Oxyprotoberberine (VI).—A boiling solution of protoberberinium chloride (0·5 g.) in water (5 c.c.) was added to a hot solution of potassium hydroxide (2·5 g.) in a little water, and the mixture heated on the steam-bath for 3 hours; the oil which separated solidified on long standing. It was usually extracted with ether, the ether removed, and the residual gum extracted several times with very dilute hydrochloric acid. By this treatment the dihydroprotoberberine present was removed, but we were not successful

in isolating the small quantities of this substance in a pure state. The residue, insoluble in dilute hydrochloric acid, was dissolved in hot glacial acetic acid and mixed with a few drops of boiling water; *oxyprotoberberine* then gradually separated and, after a second treatment with acetic acid, it was obtained pure in slender, satiny, colourless needles, m. p. 102° (Found : C, 82·6; H, 5·5. $C_{17}H_{13}ON$ requires C, 82·6; H, 5·3%). It is rather sparingly soluble in the usual organic solvents, with the exception of glacial acetic acid, and does not dissolve in dilute mineral acids. The pale yellow solution in concentrated sulphuric acid becomes pale brown on the addition of a crystal of potassium nitrate.

Tetrahydroprotoberberine Methiodides (VII).—Tetrahydroprotoberberine (5 g.) and methyl iodide (10 c.c.) were heated under reflux for ½ hour, the excess of methyl iodide was evaporated, and the solid dissolved in boiling water (250 c.c.); the *β-methiodide*, which separated on cooling, recrystallised from water in colourless prisms, m. p. 230—232° (decomp.) (Found : C, 57·2; H, 5·4. $C_{18}H_{20}NI$ requires C, 57·3; H, 5·3%). The *α-methiodide* gradually separated from the aqueous mother-liquor in colourless nodules, and crystallised from alcohol in small needles, m. p. 212° (Found : C, 57·1; H, 5·2). The *methochloride* was obtained by heating an aqueous suspension of the mixed methiodides with silver chloride. It is very soluble in water and separates as a syrup on concentration.

Anhydromethyltetrahydroprotoberberine (VIII).—Tetrahydroprotoberberine methiodide (or methochloride) was heated with excess of 10% methyl-alcoholic potassium hydroxide for 3 hours. The mixture was diluted with water, the oily base extracted with ether, dried over potassium carbonate, filtered, and the ether removed, leaving the base as an oil which did not crystallise. When triturated with dilute hydrochloric acid, it was converted into the sparingly soluble hydrochloride, and this crystallised from water in small prisms, m. p. 234—235° (decomp.), containing water of crystallisation, which is lost at 100°, the substance falling to a fine powder (Found : C, 75·0; H, 7·0. $C_{18}H_{20}NCl$ requires C, 75·6; H, 7·0%). The same base is the only ether-soluble product obtained when tetrahydroprotoberberine methiodide is treated with silver hydroxide, and the solution evaporated in a good vacuum. The ether-insoluble residue was completely soluble in water and appeared to be undecomposed *methohydroxide*. After being boiled with aqueous methyl alcohol for 4 hours, the base (VIII) was recovered unchanged and identified by conversion into the sparingly soluble hydrochloride. It was also unchanged by boiling with chloroform for 3 hours, whilst the hydrochloride was recovered after being heated with dilute hydrochloric acid on the steam-bath for 6 hours.

We wish to thank Mr. Fred Hall for carrying out the analyses required during this and the two preceding investigations. One of us (S. N. C.) desires to thank the United Provinces Government for a Scholarship which has enabled him to take part in these researches.

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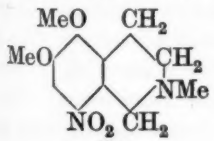
CCCV.—5 : 6-*Dimethoxy*-2-*methyl*-1 : 2 : 3 : 4-*tetrahydro*-iso*quinoline and some Derivatives.*

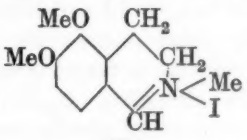
By ROBERT DOWNS HAWORTH.

THE present communication describes some experiments which were undertaken in order to discover whether the introduction of a nitro-group into a suitable position in the benzene nucleus of a 2-methyl-1 : 2 : 3 : 4-tetrahydro*iso*quinoline derivative is capable of inducing such a reactivity in the 1-methylene group as could be utilised in synthetical work connected with the *iso*quinoline alkaloids. Suitable nitro*iso*quinoline derivatives are not readily accessible, and it has been necessary to synthesise 8-*nitro*-5 : 6-*dimethoxy*-2-*methyl*-1 : 2 : 3 : 4-*tetrahydro*isoquinoline (I) in order to test the above possibility.

2 : 3-Dimethoxycinnamic acid, prepared by condensing 2 : 3-dimethoxybenzaldehyde with malonic acid, was converted into β-2 : 3-dimethoxyphenylpropionic acid by reduction with sodium amalgam (Perkin and Robinson, J., 1914, **105**, 2387). The *amide* of this acid was treated with sodium hypochlorite, and the resulting β-2 : 3-*dimethoxyphenylethylamine* converted into its N-*formyl* derivative, which yielded 5 : 6-*dimethoxy*-3 : 4-*dihydro*isoquinoline on treatment with phosphorus oxychloride. This oily base was converted to a crystalline *methiodide* (II), which was reduced by zinc dust and dilute sulphuric acid to 5 : 6-*dimethoxy*-2-*methyl*-1 : 2 : 3 : 4-*tetrahydro*isoquinoline (III), a colourless, oily base, which gave a



(I.)



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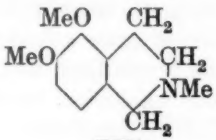
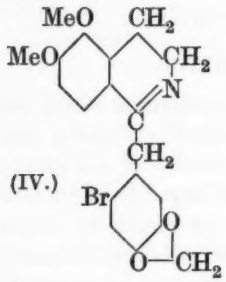


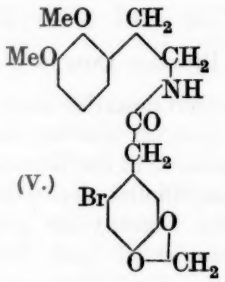
(III.)

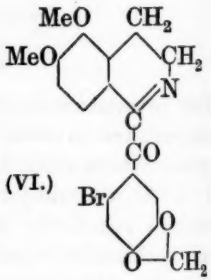
crystalline *hydriodide* and *picrate*. When this base was nitrated in glacial acetic acid it was converted into the required base (I), which,

however, did not condense with piperonal or veratraldehyde in the presence of either piperidine or methyl-alcoholic potassium hydroxide, from which it might be inferred that the effect of the nitro-group on the 1-methylene group is neutralised by the methylimino-grouping.

6′-*Bromo*-5 : 6-*dimethoxy*-3′ : 4′-*methylenedioxy*-1-*benzyl*-3 : 4-*dihydroisoquinoline* (IV) has been prepared from 3′ : 4′-*methylenedioxy*-6′-*bromophenylaceto*-β-2 : 3-*dimethoxyphenylethylamide* (V), and, like other bases of this type, it is oxidised by the air to 6′-*bromo*-5 : 6-*dimethoxy*-3′ : 4′-*methylenedioxy*-1-*benzoyl*-3 : 4-*dihydroisoquinoline* (VI) (compare Buck, Haworth, and Perkin, J., 1924, **125**, 2176).







EXPERIMENTAL.

β-2 : 3-Dimethoxyphenylpropionic acid was prepared as follows: 2 : 3-Dimethoxybenzaldehyde (10 g.), malonic acid (13 g.), pyridine (25 c.c.), and piperidine (0·5 c.c.) were heated for 1½ hours on the water-bath, then boiled for ¼ hour, and poured into dilute hydrochloric acid; the 2 : 3-dimethoxycinnamic acid was collected (yield, 95%), dissolved in 20% sodium hydroxide, and reduced at 80° with 4% sodium amalgam (200 g.). The mixture was filtered, acidified with hydrochloric acid, and the β-2 : 3-dimethoxyphenylpropionic acid collected and recrystallised from hot water (m. p. 68°).

β-2 : 3-*Dimethoxyphenylpropionamide*.—The foregoing acid (10 g.) was dissolved in chloroform (20 c.c.) and allowed to react for 1½ hours with thionyl chloride (6 c.c.) at the ordinary temperature. The mixture was poured into concentrated ammonia (50 c.c.) and water (50 c.c.), the chloroform removed by distillation, the residual liquid filtered from a little tar, and cooled; the resulting *amide* (9·5 g.) was crystallised from benzene in large, irregular prisms, m. p. 99—100° (Found: C, 62·8; H, 7·1. $C_{11}H_{15}O_3N$ requires C, 63·1; H, 7·2%), readily soluble in ether, alcohol, and hot water or benzene, but sparingly soluble in petroleum ether.

β-2 : 3-*Dimethoxyphenylethylamine*.—The amide (10 g.) was shaken with a solution of sodium hypochlorite, prepared by absorbing

chlorine (from 33 g. of potassium permanganate and concentrated hydrochloric acid) in 10% sodium hydroxide (100 c.c.). When it had dissolved, the temperature was raised to 70° for 1 hour, the solution cooled, treated with sodium hydroxide (90 g.), heated to 80° for 1½ hours, cooled, thoroughly extracted with benzene, the extract dried, the benzene removed, and the residual oil (8 g.) distilled under diminished pressure. β-2 : 3-*Dimethoxyphenylethylamine* boils at 190°/70 mm. (Found: C, 66·5; H, 8·4. $C_{10}H_{15}O_2N$ requires C, 66·3; H, 8·3%).

The *hydrochloride* is very soluble in water or alcohol, and separates as an oil on the addition of ether to the alcoholic solution. The *picrate*, prepared in alcoholic solution, crystallised from alcohol in yellow plates, m. p. 174—176° (Found: C, 47·1; H, 4·5. $C_{16}H_{18}O_9N_4$ requires C, 46·8; H, 4·4%).

5 : 6-*Dimethoxy*-3 : 4-*dihydro*isoquinoline *Methiodide* (II).—The above amine (10 g.) and anhydrous formic acid (7 g.) were heated at 180—200° for 3 hours. The resulting N-*formyl* derivative was dissolved in toluene (50 c.c.), phosphorus oxychloride (30 c.c.) added, and the mixture boiled for 1 hour; it was then diluted with petroleum ether (b. p. 40—60°), the solvent decanted from the brown gum, the latter dissolved in a little alcohol, poured into dilute hydrochloric acid, and non-basic impurities were extracted with benzene. The acid layer was made alkaline with sodium hydroxide, extracted with benzene, the extract dried over potassium carbonate, and the benzene removed, leaving 5 : 6-*dimethoxy*-3 : 4-*dihydro*isoquinoline (5 g.) as an oil which did not crystallise, but which dissolved completely in dilute hydrochloric acid to a pale yellow solution. The oil was boiled under reflux with methyl iodide, excess of the latter was removed by distillation, and the solid *methiodide* dissolved in methyl alcohol and precipitated by ether; pale yellow needles, m. p. 174—175° (Found: C, 43·3; H, 4·9. $C_{12}H_{16}O_2NI$ requires C, 43·2; H, 4·8%). This methiodide is very soluble in water and in methyl and ethyl alcohols, the yellow solutions possessing a green fluorescence.

5 : 6-*Dimethoxy*-2-*methyl*-1 : 2 : 3 : 4-*tetrahydro*isoquinoline (III).—The methiodide (II) (2 g.) was dissolved in dilute sulphuric acid, heated with excess of zinc dust on the water-bath until the solution became colourless, and filtered; the filtrate was made alkaline with ammonia, the oily base extracted with chloroform, the extract dried over potassium carbonate, and the solvent removed, whereby the *base* (III) was obtained as an oil which did not solidify on long standing. The *hydrochloride* was very soluble in water or alcohol. The *hydriodide* was obtained by adding potassium iodide to a solution of the base in dilute hydrochloric acid and recrystallising the

precipitated solid from ethyl alcohol; colourless nodules, m. p. 201° (decomp.) (Found : C, 43·2; H, 5·5. $C_{12}H_{18}O_2NI$ requires C, 43·0; H, 5·4%). The *picrate* separates from alcohol in yellow needles, m. p. 164° (decomp.).

8-*Nitro*-5 : 6-*dimethoxy*-2-*methyl*-1 : 2 : 3 : 4-*tetrahydro*isoquinoline (I).—A solution of the tetrahydro-base (1 g.) in glacial acetic acid (25 c.c.) was treated with concentrated nitric acid (2 c.c.) in acetic acid (5 c.c.) containing urea, the temperature being maintained below 20° for 4 hours. The nitration mixture was diluted with water, made alkaline with ammonia, the buff-coloured nitro-compound collected, and crystallised from aqueous methyl alcohol; almost colourless prisms, m. p. 104—105° (Found : C, 57·1; H, 6·4. $C_{12}H_{16}O_4N_2$ requires C, 57·2; H, 6·3%). The 8-*nitro*-5 : 6-*dimethoxy*-2-*methyl*-1 : 2 : 3 : 4-*tetrahydro*isoquinoline is readily soluble in the usual organic solvents, and gradually turns green on exposure to light. It was reduced with zinc dust and hydrochloric acid and filtered; the addition of ferric chloride then produced a blue coloration. Numerous unsuccessful attempts were made to condense this base with piperonal or veratraldehyde under a variety of conditions, piperidine and alcoholic potassium hydroxide being used as catalysts.

6′-*Bromo*-3′ : 4′-*methylenedioxyphenylaceto*-β-2 : 3-*dimethoxyphenylethylamide* (V) was obtained by heating molecular proportions of β-2 : 3-dimethoxyphenylethylamine and 6-bromohomopiperonylic acid at 180° for 1½ hours. The *amide* crystallised from ethyl alcohol in colourless needles, m. p. 131° (Found : C, 53·9; H, 4·8. $C_{19}H_{20}O_5BrN$ requires C, 54·0; H, 4·7%).

6′-*Bromo*-5 : 6-*dimethoxy*-3′ : 4′-*methylenedioxy*-1-*benzyl*-3 : 4-*dihydro*isoquinoline (IV) was prepared by boiling the amide (V) (5 g.) for 1½ hours with phosphorus oxychloride (15 c.c.) and toluene (25 c.c.), adding petroleum ether, and decanting the solvents from the gum. The latter was dissolved in dilute sulphuric acid, filtered from tarry material, and made alkaline with sodium hydroxide; the oily base which separated rapidly hardened, and was collected, washed with water, and crystallised from ethyl alcohol; rhombic plates, m. p. 134—135° (Found : C, 55·9; H, 4·6. $C_{19}H_{18}O_4NBr$ requires C, 56·4; H, 4·5%). Alcoholic solutions of this base were slowly oxidised on exposure to the air to 6′-*bromo*-5 : 6-*dimethoxy*-3′ : 4′-*methylenedioxy*-1-*benzoyl*-3-4-*dihydro*isoquinoline (VI), which crystallises from alcohol in colourless warts, m. p. 168° (Found : C, 54·7; H, 4·1. $C_{19}H_{16}O_5NBr$ requires C, 54·5; H, 3·8%), and gives an intense green coloration on being warmed with acetic anhydride.

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NEWCASTLE-ON-TYNE. [*Received, August 9th*, 1927.]

CCCVI.—*Investigations on the Bivalency of Carbon. Part I. The Displacement of Chlorine from Diphenylchloromethane.* s-*Tetraphenyldimethyl Ether.*

By Allan Miles Ward.

The formation of *s*-tetraphenyldimethyl ether on boiling diphenylbromomethane with water was explained by Nef (*Annalen*, 1897, **298**, 234) on the assumption that the reaction proceeded through a phase involving bivalent carbon:

$$CHPh_2Br \xrightarrow{-HBr} CPh_2< \xrightarrow{H_2O} CHPh_2\cdot OH$$
$$\qquad\qquad\qquad\quad \Big| \xrightarrow{CHPh_2\cdot OH} (CHPh_2)_2O$$

If this be so, the same considerations as those advanced for α-chloroethylbenzene (Ward, this vol., p. 445) should apply to the velocity coefficients for the displacement of the halogen atom from diphenylchloromethane. Thus the rates of displacement of the chlorine should be uninfluenced by the presence or the absence of sodium hydroxide. This is now shown to be the case for aqueous (10% by vol.) ethyl-alcoholic solutions at 25°. When sodium hydroxide is present in a concentration equivalent to the diphenylchloromethane, the velocity coefficient is that of a unimolecular reaction and of the same value as when sodium hydroxide is absent. When the concentration of the sodium hydroxide is doubled, the reaction remains unimolecular, but the velocity is somewhat decreased. A similar observation is recorded by Senter and Tucker (J., 1916, **109**, 697) for the reaction between water and the phenylbromoacetate ion.

In ethyl-alcoholic solution without added water, the presence of sodium ethoxide produced no change in the velocity of the displacement of the halogen (it was unnecessary for the alcohol to be completely anhydrous in these experiments, and lime-dried material was therefore used throughout); the presence of sodium hydroxide caused a considerable increase in the rate at 25·0°, but the reaction remained unimolecular. Observations at 35·0° in the presence and in the absence of sodium hydroxide showed similar differences, but the temperature coefficients calculated from the two sets of results were in agreement. With increasing concentration of water, the velocity of the reaction increased, being about 30 times as great when 20% of water was present as in the absolute-alcoholic solution. In the previous communication on α-chloroethylbenzene (*loc. cit.*), all velocity measurements were made in 20% aqueous-alcoholic solutions, and comparison with the velocity coefficients

of the present reaction under similar conditions shows that the halogen is displaced some 166 times more rapidly from $CHPh_2Cl$ than from CHPhMeCl.

In the kinetic experiments, the products from diphenylchloromethane were benzhydrol and diphenylmethyl ethyl ether. These conclusions are based on (1) a Zeisel determination on the products, and (2) the reaction between the products and hydrogen chloride, whereby diphenylchloromethane is re-formed from both benzhydrol and diphenylmethyl ethyl ether. In some of the experiments described, the estimation of chlorine by (2) gave low results for diphenylchloromethane, and repeated treatment with hydrogen chloride did not alter these values. In these experiments, the products were distilled at atmospheric pressure, but when all distillations were carried out under reduced pressure, the chlorine thus estimated agreed more closely with the calculated value for diphenylchloromethane. There can thus be no doubt that the low values obtained in some experiments were due to the presence of other substances formed during the distillation of the benzhydrol–diphenylmethyl ethyl ether mixture. Indeed, it was found by Goldthwaite (*Amer. Chem. J.*, 1903, **30**, 461) that *pp'*-dibromodiphenylmethyl ethyl ether on being heated at 300° decomposed entirely to *pp'*-dibromodiphenylmethane and *pp'*-dibromobenzophenone, together with a lower-boiling fraction, probably ethyl alcohol, and a gas, possibly ethylene. Bacon (*ibid.*, 1905, **33**, 92) obtained benzophenone, tetraphenylethane, and acetaldehyde on submitting diphenylmethyl ethyl ether to similar treatment. Nef (*loc. cit.*, p. 236) had previously observed that benzhydrol at 300° decomposes completely to diphenylmethane, benzophenone, and tetraphenylethane. The analytical results would point, however, to the decomposition of the ether being very much less at atmospheric pressure than that of the benzhydrol. The Zeisel determinations are of interest in showing that some 8% of benzhydrol is formed when lime-dried alcohol is used, this no doubt being due to the water present in this solvent. In aqueous (10% by vol.) ethyl-alcoholic solution, the proportion of benzhydrol formed is higher in the absence of sodium hydroxide than in its presence, being 18% and 14%, respectively, and this provides further evidence that hydroxyl ions are not directly active in the substitution.

The reaction mechanism derived from the kinetic results and from the products of reaction may thus be stated

$$CHPh_2Cl \longrightarrow CPh_2< + HCl \text{ (slow)}$$
$$CPh_2< + H_2O \longrightarrow CHPh_2{\cdot}OH \text{ (rapid)}$$
$$CPh_2< + EtOH \longrightarrow CHPh_2{\cdot}OEt \text{ (rapid)}$$

exactly as for α-chloroethylbenzene, and no experimental results are obtained contrary to Nef's hypothesis that the reaction proceeds through the phase $CPh_2<$.

It is shown also that *s*-tetraphenyldimethyl ether may be formed with ease from benzhydrol by boiling it under reflux with hydrochloric acid, just as, under similar conditions, αα′-diphenyldiethyl-ether and styrene are formed from phenylmethylcarbinol (Ward, *loc. cit.*). If the former reaction proceeds through the phase $CPh_2<$ as postulated, no unsaturated hydrocarbon of the styrene type could be formed, and the ether was, in fact, the only product isolated. The effects of varying the times of heating at 100° and of altering the concentration of hydrochloric acid were observed in relation to the proportion of ether formed. With increasing concentration of hydrochloric acid, the proportion of ether formed passed through a maximum, and the amount of diphenylchloromethane increased from zero at first, until, with concentrated acid, it became the main product of reaction. Conversely, when *s*-tetraphenyldimethyl ether was boiled with concentrated hydrochloric acid, diphenylchloromethane was the main product, whereas with *N*/2-acid no change occurred. Moreover, it was found in these experiments that when the products were distilled and then treated with hydrogen chloride, values for the chlorine content were obtained which were too low for diphenylchloromethane. This was doubtless due to the decomposition of the original products of reaction on distillation, as in the case of the benzhydrol–diphenylmethyl ethyl ether mixtures (p. 2286). Thus Nef (*loc. cit.*, p. 236) found that *s*-tetraphenyldimethyl ether on being heated at 300° decomposed to benzophenone, diphenylmethane, and tetraphenylethane. In the present experiments, the products of distillation were not systematically examined except in the case of one experiment with *s*-tetraphenyldimethyl ether, in which diphenylmethane was isolated. The presence of this as a product of secondary decomposition would account for the anomalous chlorine results. When the products of the reaction between concentrated hydrochloric acid and benzhydrol or *s*-tetraphenyldimethyl ether were examined by methods avoiding distillation or heating at higher temperatures, no evidence was obtained for the formation of any substances other than diphenylchloromethane, benzhydrol, and *s*-tetraphenyldimethyl ether.

Although the results find a complete explanation on the basis of Nef's hypothesis, other interpretations may possibly be formulated. Thus assuming that diphenylchloromethane reacts in virtue of its ions as in (1)—(4), the kinetic results would then necessitate

that (1) should be a time reaction and (2) and (3) extremely rapid.

(1) $CHPh_2Cl \longrightarrow CHPh_2^{\cdot} + Cl'$
(2) $CHPh_2^{\cdot} + OH' \longrightarrow CHPh_2{\cdot}OH$
(3) $CHPh_2^{\cdot} + OEt' \longrightarrow CHPh_2{\cdot}OEt$
(4) $CHPh_2^{\cdot} + OCHPh_2' \longrightarrow (CHPh_2)_2O$

Although an increase in the hydroxyl-ion concentration from about 10^{-8} (in 10% aqueous ethyl-alcoholic solution) to 0·176 (in the presence of sodium hydroxide) would thus greatly increase the velocity of (2), it would not affect the measured velocity, which *ex hypothesi* depends solely on (1). Also, from the equilibrium $EtOH + OH' \rightleftharpoons OEt' + H_2O$, an increase is seen to take place in the ethoxyl-ion concentration parallel with that in the hydroxyl-ion concentration, but the increased velocity of (3) would not influence the measurable velocity. Slowness of (1) and rapidity of (2) and (3) would be almost inevitably connected, since each represents the very slight tendency for the formation of $CHPh_2^{\cdot}$ ions. The same considerations hold concerning phenylmethylcarbinol (*loc. cit.*). Should the reaction in this case proceed through the phase $CHPhMe^{\cdot}$, it must be assumed that this is capable of losing a hydrogen ion in order to account for the production of styrene. The halogen displacement from the triarylmethyl chlorides may be assumed to take place as in (1), but the hexaaryldimethyl ethers have not been prepared by this method (compare Gomberg, *J. Amer. Chem. Soc.*, 1913, **35**, 200). In this connexion an examination of systems of the type $CR_1R_2R_3Cl$ should provide valuable data.

Experimental.

Diphenylchloromethane was prepared from benzhydrol by means of hydrogen chloride in benzene solution (Böeseken, *Rec. trav. chim.*, 1903, **22**, 313; Montagne, *ibid.*, 1906, **25**, 405) and was obtained as a colourless liquid, b. p. 158·5—159·5°/12 mm., which solidified to a colourless solid, m. p. 20·5° (Engler and Berthge, *Ber.*, 1874, **7**, 1128, give m. p. 14°, and Böeseken gives m. p. 12—14°). It was kept in small sealed glass tubes, for turbidity developed rapidly in contact with the atmosphere. The chlorine was determined (i) by heating a weighed sample in aqueous ethyl alcohol and titrating the liberated acid with standard alkali until the colour change of the indicator (phenolphthalein) was permanent (Found : Cl, 17·64. Calc. : Cl, 17·53%), and (ii) by Stepanow's method (Found : Cl, 17·47%). In all subsequent analyses, the chlorine was estimated as under (i).

Diphenylchloromethane was also prepared by suspending *s*-tetraphenyldimethyl ether (90 g.) in benzene (180 c.c.) and passing in a rapid stream of hydrogen chloride for 1 hour at room temperature. The ether dissolved completely and an aqueous layer formed; this was separated and the benzene solution dried by means of calcium chloride. The hydrogen chloride was removed in a current of carbon dioxide, and the product, b. p. 165·5°/15 mm., collected; yield, 88 g. (Found: Cl, 17·57%). Some tar remained in the distilling flask.

Products of the Reaction of Diphenylchloromethane and Ethyl Alcohol.—(*a*) Ethyl alcohol (250 c.c.), dried by refluxing and distilling over quick-lime, was added to diphenylchloromethane (5 g.). The solution was maintained at 25° for 5 days, free hydrogen chloride was then removed by means of potassium carbonate, and the alcoholic solution fractionated, 4·9 g. of liquid, b. p. 146—147°/9 mm., being obtained (Nef, *loc. cit.*, p. 234, gives b. p. 153°/15 mm. for diphenylmethyl ethyl ether) (Found: OEt, 19·6. Calc. for diphenylmethyl ethyl ether: OEt, 21·2%). The product redistilled at 281°/766 mm. (Kostanecki and Lampe, *Ber.*, 1906, **39**, 4019, give b. p. 288°) (Found: OEt, 19·2%).

(*b*) Repetition of this experiment with 15 g. of diphenylchloromethane and 500 c.c. of alcohol for 10 days gave 14·2 g., b. p. 115—119°/4 mm. (Found: OEt, 19·5, 19·4%).

(*c*) Hydrogen chloride was passed through the liquid obtained in (*a*) at room temperature. Considerable heat was developed, and after some time separation into two layers took place. Calcium chloride was added, and after standing, the products, which remained heterogeneous, were distilled. On heating, appreciable charring and marked evolution of gas took place, the material then distilling smoothly, b. p. 156—158°/11 mm. (Found: Cl, 16·1. Calc. for diphenylchloromethane: Cl, 17·53%).

(*d*) 5 G. of the product from (*b*) were dissolved in benzene (15 c.c.) and hydrogen chloride was passed in rapidly for 2 hours. Two layers were again formed and remained after drying by means of calcium chloride. The hydrogen chloride was removed in a stream of carbon dioxide, the benzene distilled under diminished pressure, and a colourless liquid obtained (4·2 g.), b. p. 120—121°/3 mm. (Found: Cl, 17·25%). Considerable dark brown gum remained in the distilling flask.

Products of the Reaction of Diphenylchloromethane with Aqueous Ethyl Alcohol.—(*e*) A solution of diphenylchloromethane (5 g.) in ethyl alcohol (225 c.c.) and water (25 c.c.) was kept at 25° for 12 hours, the water then removed by means of potassium carbonate, and the products distilled, giving 4·5 g. of liquid, b. p. 113—120°/3

mm., which redistilled at 281—288°/766 mm. (Found : OEt, 17·8%), some charred material remaining in the distilling flask. The liquid was dissolved in petroleum ether and treated with hydrogen chloride as under (*c*) above, a fraction of b. p. 162—163°/16 mm. (Found : Cl, 16·58%) being obtained.

(*f*) Ethyl alcohol (1125 c.c.), water (125 c.c.), and diphenylchloromethane (25 g.) were treated as in (*b*) and gave 21·5 g., b. p. 125—130°/3 mm. (Found : OEt, 17·3, 17·4%). Treatment of a sample (5 g.) as under (*d*) above, gave 4·4 g. of colourless liquid, b. p. 115°/1 mm. (Found : Cl, 17·22%). Some gum remained in the distilling flask.

Products of the Reaction of Diphenylchloromethane with Aqueous Ethyl-alcoholic Sodium Hydroxide.—(*g*) Diphenylchloromethane (5 g.) was dissolved in ethyl alcohol (225 c.c.) and aqueous 1·76*N*-sodium hydroxide (25 c.c.). The solution was kept at 25° for 12 hours, dried, and the liquid distilled, b. p. 116—124°/3 mm.; yield, 4·3 g. The products redistilled at 279—285°/766 mm. (Found : OEt, 18·2%). After treatment with hydrogen chloride in benzene solution, the liquid distilled at 156—158°/11 mm. (Found : Cl, 16·6%). This product was again treated with hydrogen chloride, but the chlorine content remained unchanged.

(*h*) The water in Expt. (*f*) was replaced by the same volume of aqueous 2*N*-sodium hydroxide and the same procedure followed; yield, 21·5 g.; b. p. 114—121°/3 mm. (Found : OEt, 18·2, 18·1%). A small amount of gum remained in the distilling flask. Treatment of a sample (5 g.) as under (*d*) above, gave 4·3 g. of a colourless liquid, b. p. 121—124°/4 mm. (Found : Cl, 17·29%). A small amount of brown oil remained in the distilling flask.

Reaction between Benzhydrol and Hydrochloric Acid.—In each experiment benzhydrol (5 g.) and hydrochloric acid of the normality stated were heated in a pressure flask immersed in a bath of boiling water for the times shown in the following table. The products solidified on being poured into cold water, and the *s*-tetraphenyldimethyl ether and benzhydrol were then readily separated by dissolving the mixture in hot alcohol, the main bulk of the ether crystallising in a pure condition on cooling. Addition of a little water to the alcoholic mother-liquor precipitated a mixture of the ether and benzhydrol, which was separated into its components by a repetition of this process, whilst by the addition of the aqueous alcoholic solution to excess of water, the benzhydrol was obtained in a pure condition. The purity of the benzhydrol (m. p. 68°) and of the *s*-tetraphenyldimethyl ether (m. p. 110°) was checked in these and in all subsequent experiments by determining the m. p.'s both alone and when mixed with authentic specimens. In the

		Yields, g.				Yields, g.	
HCl, *N*.	Time (hrs.).	Ether.	Benz-hydrol.	HCl, *N*.	Time (hrs.).	Ether.	Benz-hydrol.
0·5	1	—	5·0	1	6	2·1	2·3
0·5	4	1·2	3·5	2	1	1·55	3·0
0·5	8	1·75	2·85	2	6	3·5	0·75
0·5	20	2·55	2·4	3·5	1	3·6	0·95
1	1	0·8	4·05	3·5	6	3·9	—

final experiment, no precipitate but only a turbidity was formed on adding the aqueous alcoholic solution to excess of water. In several of the preceding experiments, mainly those in which the higher concentrations of acid were used or in which the times of heating were longer, the total yield of ether and carbinol was lower than the theoretical, and in these cases the filtrate after separation of the benzhydrol was turbid, doubtless due to the partial formation of diphenylchloromethane, as shown in the following experiments.

(*i*) Benzhydrol (5 g.) and 5*N*-hydrochloric acid (75 c.c.) were heated in a pressure flask at 100° for 1 hour. The products on being poured into cold water solidified to a pasty mass. On the addition of petroleum ether (b. p. 40—60°), a white solid was at once obtained, which on crystallisation from alcohol gave *s*-tetraphenyldimethyl ether (2·2 g.). Dilution of the alcoholic filtrate with water produced a turbidity only. The petroleum-ether solution was dried, and the solvent evaporated completely at room temperature, a pasty mass (2 g.; Cl, 7·7%) thus being obtained.

(*j*) Benzhydrol (10 g.) was boiled under reflux with concentrated hydrochloric acid (100 c.c.) for 2 hours. The oil, which did not solidify on cooling, was extracted with ether, dried and distilled; b. p. 160—161°/15 mm.; yield, 7·85 g.; Cl, 15·4%. A black gum remained in the distilling flask. In a second experiment, with only 1 hour's boiling, the following results were obtained: b. p. 159—161°/14 mm.; yield 7·6 g.; Cl, 15·2%; whilst in a third experiment, the reaction being carried out in a pressure flask immersed in a bath of boiling water for 1 hour, 7·4 g. of product (Cl, 14·9%) were obtained. This was dissolved in benzene, saturated with hydrogen chloride, and on distillation gave a liquid, b. p. 156—158°/12 mm. (Cl, 14·7%).

(*k*) Benzhydrol (50 g.) was boiled under reflux with concentrated hydrochloric acid (500 c.c.) for 2 hours. The cooled products were extracted with ether, dried, and the ether distilled under diminished pressure at room temperature. The oil (50 g.; Cl, 15·3%) so obtained was dissolved in some 250 c.c. of petroleum ether (b. p. 40—60°), but no solid separated on standing. The petroleum ether was completely removed by distillation at room temperature, excess of water added, and the mixture maintained at 25° for 3 weeks with

occasional shaking. The displacement of the halogen at the end of this period was still incomplete, and the mixture was therefore gently warmed until no further acidity developed. On cooling, the products solidified to a hard mass, which was filtered, washed with water, and dried (yield 45·5 g.). Crystallisation from petroleum ether gave a crop of 41·6 g., yielding benzhydrol (20·9 g.) and *s*-tetraphenyldimethyl ether (20·3 g.). From the petroleum-ether liquors on evaporation at room temperature a solid (3·35 g.) was obtained; on recrystallisation from petroleum ether, this gave a product (2·5 g.) which was separated into benzhydrol (0·8 g.) and *s*-tetraphenyldimethyl ether (1·6 g.). The residual liquors on evaporation at room temperature gave a small amount of solid, from which 0·1 g. of the ether was separated, and a yellow oil (*ca.* 0·5 c.c.) which completely decomposed on attempted distillation.

Reaction between s-*Tetraphenyldimethyl Ether and Hydrochloric Acid.*—(*l*) *s*-Tetraphenyldimethyl ether (10 g.) and *N*/2-hydrochloric acid (150 c.c.) were boiled under reflux for 8 hours. Solid was present all the time and 9·9 g. of ether were recovered.

(*m*) *s*-Tetraphenyldimethyl ether (50 g.) and concentrated hydrochloric acid (500 c.c.) were boiled under reflux for 1 hour. The products were cooled, extracted by ether, dried, and the solvent was removed on the water-bath. During the heating, the liquid darkened considerably (Found: Cl, 6·54%). The products on inoculation with *s*-tetraphenyldimethyl ether solidified to a stiff paste, which was filtered and washed with petroleum ether (b. p. 40—60°), *s*-tetraphenyldimethyl ether (10·5 g.) being thus obtained pure. The filtrate was distilled under diminished pressure, b. p. 145—170°/12 mm.; yield 25 g. (Found: Cl, 10·5%). A considerable amount of dark brown gum remained in the distilling flask, but the only product which was separated from this was *s*-tetraphenyldimethyl ether (1·7 g.). The above distillate (25 g.) was boiled with water for ½ hour (reflux), but remained liquid on cooling. Addition of petroleum ether yielded a solid (6·7 g.) which gave benzhydrol (5·9 g.) and *s*-tetraphenyldimethyl ether (0·4 g.). The petroleum-ether solution was dried and distilled; b. p. 146—160°/14 mm.; yield, 10 g. A considerable amount of oil, which solidified to a hard mass, remained in the distilling flask, and this on crystallisation from alcohol gave *s*-tetraphenyldimethyl ether (3 g.). Phenylhydrazine (7 g.) and alcohol (20 c.c.) were added to the distillate (10 g.) and the solution was refluxed for 9 hours, but even on cooling it remained homogeneous, thus showing benzophenone to be absent. Excess of dilute hydrochloric acid was added and the products were distilled in steam; a pleasant-smelling oil was obtained, which was extracted with ligroin, dried, and distilled,

giving fractions (1) b. p. 129—135°/11 mm., 2 c.c.; (2) b. p. 135—155°/11 mm., 4 c.c.; a small amount of liquid remained. An authentic specimen of diphenylmethane distilled at 129—130°/11 mm., and remained liquid for a considerable time after distillation, but on seeding solidified to a hard mass of long, colourless needles. Fraction (1) was similarly treated, and its behaviour was identical.

(*n*) *s*-Tetraphenyldimethyl ether (50 g.) and concentrated hydrochloric acid (500 c.c.) were boiled under reflux for 4 hours. The cooled products were extracted by ether, dried, and the solvent was removed under diminished pressure at room temperature during 7 hours; yield 47·5 g. (Found: Cl, 12·4%). The addition of petroleum ether caused a colourless solid (6·2 g.) to separate on standing, giving *s*-tetraphenyldimethyl ether (5·7 g.) and benzhydrol (0·25 g.). The petroleum ether was removed under diminished pressure at room temperature, and the colour of the products darkened, although to a very much less degree than in the preceding experiment; yield, 40·5 g. (Found: Cl, 14·2%). The replacement of the halogen was carried out exactly as in the corresponding benzhydrol experiment, a colourless, crystalline solid (37 g.) being obtained. On crystallisation from light petroleum, this gave a crop (31 g.) which yielded *s*-tetraphenyldimethyl ether (11 g.) and benzhydrol (19·5 g.). On evaporation of the liquors at room temperature a pasty solid was formed, which was washed with petroleum ether; 3·5 g. remained, yielding 3·3 g. of *s*-ether. The liquors on evaporation gave 2·3 g. of oil, which, since it still contained diphenylchloromethane, was boiled with water; on cooling, it solidified to a pasty solid, from which were separated *s*-ether (0·7 g.) and benzhydrol (0·8 g.), whilst the distillate from the small quantity of residual oil was insufficient for further examination.

Kinetic Experiments.

In the following experiments, a weighed amount of diphenylchloromethane was dissolved in ethyl alcohol (prepared by refluxing and distilling commercial absolute alcohol over quick-lime); the required amounts of water (by volume) and of sodium hydroxide or sodium ethoxide solutions were added, at the temperature of experiment, and the volume in each case was made up to 100 c.c. with ethyl alcohol. The method of experiment was that described previously (*loc. cit.*, p. 455) and the results are expressed as before, except that titrations refer to 10 c.c. of solution against alcoholic sodium hydroxide ($N/20$) or alcoholic benzoic acid ($N/20$). In each case k is calculated from the formula $k = 2{\cdot}3/t \,.\, \log_{10} a/(a - x)$ for a unimolecular reaction, t throughout being expressed in minutes, and a being based on the first titre. Typical experiments showing

the extent of the variations amongst the individual values of k are given (1 and 2), and the complete results are then summarised.

(1) Diphenylchloromethane, 0·0906 mol./l.; water, 10% (by vol.); temp. 25·0°.

t.	Titre.	k.	t.	Titre.	k.
4	1·47	—	64	15·23	0·0294
14	5·87	0·0307	84	16·60	0·0301
24	8·87	0·0294	144	17·94	—
44	13·01	0·0296	1350	18·09	—

(2) Diphenylchloromethane, 0·0818 mol./l.; sodium hydroxide, 0·0880 mol./l.; water, 10% (by vol.); temp. 25·0°.

t.	Titre.	k.	t.	Titre.	k.
3	15·98	—	63	3·46	0·0301
13	12·32	0·0280	83	2·46	0·0291
23	9·40	0·0289	279	1·06	—
43	5·62	0·0294	1260	1·00	—

(3) Temp. 25·0°.

$CHPh_2Cl$ (mol./l.).	Water (% by vol.).	NaOH (mol./l.).	NaOEt (mol./l.).	k.
0·0696	—	—	—	0·00341
0·0781	—	—	—	0·00349
0·0974	—	—	0·1297	0·00345
0·1167	—	—	0·2407	0·00354
0·1059	—	—	0·2315	0·00343
0·0733	—	0·0914	—	0·00395
0·0764	1	—	—	0·00468
0·0956	2	—	—	0·00638
0·1054	5	—	—	0·0115
0·0906	10	—	—	0·0298
0·0776	10	—	—	0·0294
0·0818	10	0·0880	—	0·0291
0·0811	10	0·0880	—	0·0293
0·0878	10	0·1760	—	0·0272
0·0845	10	0·1760	—	0·0277
0·0795	20	—	—	0·103

(4) Temp. 35·0°.

$CHPh_2Cl$ (mol./l.).	Water (% by vol.).	NaOH (mol./l.).	k.	Temp. coeff. (10°).
0·0828	—	—	0·0101	2·98
0·0867	—	—	0·0101	
0·1942	—	—	0·0104	
0·0980	—	0·0982	0·0117	2·95
0·0818	—	0·1848	0·0116	

Summary.

(1) The displacement of the halogen from diphenylchloromethane at 25° in ethyl-alcoholic solution (lime-dried) and in aqueous ethyl-alcoholic solutions, both alone and in the presence of sodium hydroxide, yields a mixture of diphenylmethyl ethyl ether (main product) and benzhydrol.

(2) The velocity coefficients obtained for this displacement in ethyl-alcoholic solution alone, and also in the presence of sodium hydroxide and of sodium ethoxide, at 25° and at 35°, are those of a unimolecular reaction, the sodium hydroxide, sodium ethoxide, or their ions playing no direct part in the halogen displacement. Similar results are obtained in aqueous-alcoholic solutions.

(3) Benzhydrol gives *s*-tetraphenyldimethyl ether in good yield on being boiled with dilute hydrochloric acid. With increasing concentration of acid, the yield of *s*-tetraphenyldimethyl ether passes through a maximum, and the yield of diphenylchloromethane rises, becoming the main product of the reaction when concentrated acid is used.

(4) *s*-Tetraphenyldimethyl ether is unchanged on boiling with *N*/2-hydrochloric acid, but with concentrated acid it is largely converted to diphenylchloromethane. Diphenylchloromethane may be prepared readily in a pure condition and in good yield by the action of hydrogen chloride on *s*-tetraphenyldimethyl ether suspended in benzene.

(5) The experimental evidence under (1), (2), (3), and (4) is in accordance with the hypothesis of Nef that the reactions proceed through a phase $CPh_2<$, in which but two groups are momentarily attached to carbon. An alternative mechanism involving the $CHPh_2^{\bullet}$ ion is also discussed.

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CCCVII.—*The Determination of Dissociation Constants of Dihydric Mono- and Di-nitrophenols Electrometrically and Colorimetrically.*

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THE conductivities were determined by the Kohlrausch method in a gas-regulated thermostat which was maintained at 25·0° ± 0·05°. The cell constant, as determined by solutions of *N*/10- and *N*/100-potassium chloride and saturated calcium sulphate, was 0·298. The conductivity water had a specific resistance of $4—5 \times 10^{-6}$ reciprocal ohm. The conductivities were corrected for that of the water by the usual method (Ostwald and Luther, "Physico-

chemical Measurements ") at the highest dilutions, when necessary. The trustworthiness of the apparatus was tested by determining the conductivity of acetic acid, with the following results :

At v =	16	32	64	128	256
$K \times 10^6$ =	18·33	18·56	18·47	18·36	18·50

The colorimetric measurements were carried out in a small colour comparator, in daylight, and in the manner already described (J., 1924, **125**, 2110; 1925, **127**, 2499).

The Preparation and Properties of the Compounds, and the Determination of their Constants.

2 : 6-*Dinitroquinol.*—The preparation and properties of this compound have already been described (J., 1924, **125**, 2110). The dissociation constant determined by Bader (*Z. physikal. Chem.*, 1890, **6**, 287), when multiplied by 10^{-2} in order to render it comparable with the more usual mode of expression, was $0{\cdot}7 \times 10^{-4}$, at dilutions from 200 to 1600. Bader's value of λ_0, translated into modern units, is 376, whereas we find that λ_0 of the dinitro-acid is 380. It was decided to repeat the measurements of this compound for this reason and for others, among which were the circumstances that it was evidently sensitive to catalytic oxidation and that the purity of some of Bader's preparations had been questioned by subsequent workers (*e.g.*, Walker and Cormack, J., 1900, **77**, 5).

Solutions freshly made from the calculated weights of either the hydrated or the anhydrous compound were found to have the same conductivities. When they were allowed to stand in contact with the electrodes for some time, the colour changed from red to yellowish-brown, the conductivity altered, and the characteristic purple colour then no longer appeared on the addition of alkali. These changes are probably due to oxidation. The colour also changed when hydrogen was passed over the electrode, and finally a black precipitate appeared; thus reduction also probably takes place. Solutions were freshly made for each determination of conductivity, the dilutions being performed outside the cell, because it was soon evident that these changes in their first stages were accompanied by a diminution in the resistance in the more dilute, as well as in the more concentrated, solutions. Three independent series of measurements were first made, and the constants calculated in the usual manner.

	First series.				Second series.			Third series.	
v =	184	368	736	1472	203	406	812	562	1124
λ =	60·2	70·0	81·8	101	66·6	76·8	85·8	74	93·2
$K \times 10^4$ =	1·62	1·13	0·80	0·655	1·83	1·26	0·81	0·83	0·71

In the fourth series, measurements were made after 20, 40, and 60 secs., and the readings were extrapolated to zero time; for instance, in one case the resistances of the solution in the cell were 1975, 1940, and 1920 ohms, respectively. Hence, at zero-time the resistance was 2010 ohms and the constant $1{\cdot}72 \times 10^{-4}$.

v =	221	442	884	1768
λ =	67·2	80	89·5	106·5
α =	0·177	0·211	0·236	0·280
$K \times 10^4$ =	1·72	1·27	0·824	0·614

There is thus an undoubted diminution of the constant with dilution, in the direction usually observed in the case of acids of medium strength, although 2 : 6-dinitroquinol is not sufficiently strong to be included in this class, which might, however, include the strongest of the acids investigated. In the case of 2 : 6-dinitroquinol, we suspect that the anomalous behaviour is connected with the transition into the second, or red, quinonoid form, for, at the p_H produced by the dissociation of the compound itself in water, this transition would have proceeded to a considerable extent. Pending an explanation, we have adopted a mean constant of 1×10^{-4}, $p_K = 4{\cdot}0 \pm 0{\cdot}2$, for comparison with the other compounds.

3 : 5-*Dinitropyrocatechol.*—This compound, as previously described (J., 1925, **127**, 2499), appears as bright yellow crystals, m. p. 164°. The conductivity of the solutions did not alter on standing in contact with the electrodes. Three series of readings gave :

At v =	890	1010	1010	1780	2020	2020	3560	4040	4040
λ =	149·5	162·5	160·0	190	204	200	228	243	243·5
$K \times 10^4$ =	2·88	3·17	3·09	2·80	3·10	2·92	2·54	2·8	2·8

The mean value of K is $2{\cdot}9 \times 10^{-4}$, $p_K = 3{\cdot}54$.

2 : 4-*Dinitroresorcinol.*—2 : 4-Dinitrosoresorcinol, prepared according to the method of Fitz (*Ber.*, 1875, **8**, 631), was treated with cold concentrated nitric acid (Kostanecki and Feinstein, *Ber.*, 1888, **21**, 3121) in a freezing mixture to minimise the formation of styphnic acid, any of which was removed by shaking with a large quantity of water. The nitro-compound appeared as light yellow crystals, m. p. 142°. The solution was quite stable in contact with the electrodes. Two series of measurements were made, in each of which a distinct diminution of the constant with increasing dilution was observed. Since this is by far the strongest acid of the series, we consider that this diminution may be due to the same causes as that found in the case of acids of medium strength.

	First series.						Second series.				
v =	190	380	760	1520	3040	6080	240	480	960	1920	7680
λ =	129	162	200	236	262	265	141·5	177	215	248	273
$K \times 10^4$ =	9·22	8·43	8·47	6·74	5·05	4·70	9·29	8·47	7·73	6·44	2·69

In accordance with the usual practice, we have excluded values

obtained at a degree of primary ionisation greater than 0·5 ($v > 700$). The mean value of K is $8{\cdot}85 \times 10^{-4}$, $p_K = 3{\cdot}05$.

The compound is colourless in acid solution, and full yellow from about p_H 6·65. There is no further colour change in more strongly alkaline solution up to p_H 12. The colorimetric degrees of transformation were investigated by the methods which are described in the two former papers (*loc. cit.*). The values were found, however, to vary with the p_H of the standard buffer solution containing the partly transformed compound, thus

At p_H =	3·69	3·37	4·2
p_K =	4·09	3·85	4·3

None of the other compounds investigated shows such variations. The colorimetric constant can therefore only be roughly defined as $3{\cdot}9 \pm 0{\cdot}4$—the mean of many determinations at various concentrations. The colour change is very gradual; thus no difference in colour between solutions of p_H 4·77 and 5·07, each containing 8 drops of $M/20$-solution of the compound (in alcohol), can be detected by visual matching.

4 : 6-*Dinitroresorcinol.*—This compound, prepared as already described (*loc. cit.*, 1925), forms yellow prisms, m. p. 214·5°. It is the least soluble of all the compounds investigated. The solutions were quite stable when in contact with the electrodes. The bridge settings were not quite so accurate at these high dilutions and resistances. The last value was not used in calculating the constant, since the corresponding degree of ionisation was 0·68.

v =	2560	5180	5180	10,360
λ =	163	198	188	257
$K \times 10^4$ =	1·22	1·09	0·94	1·39

The mean value of K is $1{\cdot}05 \times 10^{-4}$, $p_K = 3{\cdot}98$.

The solubility of the compound was found to be 0·0781 g. per litre by means of a conductivity titration, using a method which we hope to describe in a further communication.

The mobility of the dinitro-anion was determined by means of the monosodium salt. An $N/61{\cdot}9$-solution ($v_1 = 61{\cdot}9$) was diluted in steps of 2, the corresponding values of λ_1, etc., being treated by the well-known formula derived from the graph of λ and $\sqrt[3]{C}$ in order to obtain λ_0 (Kohlrausch, "Das Leitvermögen der Elektrolyte").

λ_1	λ_2	λ_4	λ_8	λ_{16}	λ_{32}
68·4	72·1	74·9	76·75	78·6	79·9

Hence $\lambda_0 = 2\lambda_8 - \lambda_1 = 85{\cdot}1$, etc.; the mean value was 85·0. The same results were also treated by the method of Ferguson and Vogel (*Phil. Mag.*, 1925, **50**, 971). In the equation

$$\log \delta\lambda = n \log C - \log B(1 - r^n),$$

in which C is the concentration, $\delta\lambda$ the difference in λ brought about by the dilution in the common ratio "r" (in this case 2), the constants n and B were found to be $n = 0{\cdot}437$, $B = 90{\cdot}9$. Hence λ_0 from the individual values of $\delta\lambda$ was 83·08 (82·8—83·2). The compound therefore behaves quite normally like a salt of a strong base and a strong acid. For several reasons we have preferred the value of λ_0 as given by the usual method. Combining this with the limiting mobility of $Na^{\cdot} = 51$, we find that of the anion to be 34, and that of the free monobasic acid 381.

Nitroquinol.—The sample consisted of dark red crystals, m. p. 128° (*loc. cit.*, 1924). The solutions, like those of dinitroquinol, changed in conductivity on standing in contact with the electrodes. Dilutions were therefore made outside the cell, and measurements were taken quickly. The two values of λ refer to two experiments at each dilution. The conductivity can be restored to nearly its original value by passing hydrogen over the electrodes.

v =	127	248	254	496	508
λ =	4·2 (4·74)	6·07 (6·31)	5·7 (7·25)	9·88 (10·2)	7·06 (7·74)
$K \times 10^6$ =	0·981	1·13	0·92	1·41	0·701

The values in brackets are given as showing the variability introduced by a slight delay in taking measurements. The constant is calculated from the lowest values of λ in each case. The mean constant is $1{\cdot}01 \times 10^{-6}$, $p_K = 6{\cdot}0$.

3-*Nitropyrocatechol.*—This was prepared by a modification of the method of Weselsky and Benedickt (*Monatsh.*, 1882, **3**, 386). The mixture of the 3- and 4-isomerides with unchanged pyrocatechol was distilled with steam. The distillate, containing the pyrocatechol and the 3-isomeride, was extracted with ether. The residue from this extraction was further extracted with boiling light petroleum. The 3-isomeride was obtained as bright yellow needles, m. p. 86°. Solutions kept in contact with the electrodes change in conductivity: the change is accelerated by passing oxygen and retarded by passing hydrogen. The precautions already mentioned were taken.

	First series.				Second series.	
v =	65·4	130·8	261·6	523·2	184	736
λ =	4·15	6·08	7·42	10·3	6·1	17·4
$K \times 10^6$ =	1·87	1·99	1·50	1·45	1·45	3·01

The mean value of K is $1{\cdot}88 \times 10^{-6}$, $p_K = 5{\cdot}73$.

The compound is colourless in acid solution, and full yellow at p_H 7·8—10·0. At higher values of p_H, there is a second change, to red-brown, becoming purple at about p_H 13—14. The colorimetric constants were determined by the methods already described:

$${}_1K = 1 \times 10^{-5},\ p_{K_1} = 4{\cdot}95;\ {}_2K_c = 0{\cdot}93 \times 10^{-11},\ p_{K_2} = 11{\cdot}03.$$

4-*Nitropyrocatechol.*—The method of Weselsky and Benedickt gives a product mixed with tarry matter. A more satisfactory method is that of Benedickt (*Ber.*, 1878, **11**, 362). The product when recrystallised from hot benzene is light brown, m. p. 173°. The conductivity of the solutions increased when they were in contact with the electrodes; the lower value of λ was therefore used in calculating the constants.

v =	48·1	51·5	96·2	192·4	384·8
λ =	1·51 (1·77)	1·72	1·97 (2·14)	2·25 (2·49)	5·22 (6·00)
$K \times 10^7$ =	3·33	4·05	2·83	1·85	5·02

The mean value of K is $3{\cdot}52 \times 10^{-7}$, $p_K = 6{\cdot}45$.

The compound is faintly yellow even in acid solution. It changes to red and ultimately to purple with increasingly alkaline solutions.

The constant of the first colour change was determined as already described. The second colorimetric constant was determined by comparison of a tube containing 5 drops at p_H 7·25 (full yellow) behind one containing 5 drops at p_H 13·76 (red) with one containing 10 drops, which matched when p_H was adjusted to 10·96. In another experiment, 8 drops of the solution of 4-nitropyrocatechol in a known p_H (10·64), were matched by 2 drops (in red solution) plus 6 (in yellow). The mean constants are $K_1 = 2{\cdot}8 \times 10^{-6}$, $p_{K_1} = 5{\cdot}56$; $K_2 = 1{\cdot}1 \times 10^{-11}$, $p_{K_2} = 10{\cdot}96$. An M/20-alcoholic solution was used.

2-*Nitroresorcinol.*—The method of preparation and the determination of the colorimetric constants have already been described (*loc. cit.*, 1925). The compound appeared as bright red crystals which melted sharply at 83·5°. Since the compound and its sodium salt are quite stable in solution, the latter was used in the determination of the mobility of the mononitro-anion, in the manner described above. Solutions were diluted in the cell, each dilution being two-fold, and the initial dilution, corresponding to λ_1, being 33·8.

λ_1	λ_2	λ_4	λ_8	λ_{16}	λ_{32}
66·2	69·7	72·9	75·9	77·1	78·8

Hence $\lambda_0 = 2\lambda_8 - \lambda_1 = 85{\cdot}6$, etc., the mean of the values of λ_0 being 84·9.*

* The degree of hydrolysis is inappreciable at all dilutions except the highest (v = *ca.* 1000). Taking K as $1{\cdot}6 \times 10^{-6}$, we find by the usual formula that the degree of hydrolysis is $2{\cdot}24 \times 10^{-3}$. The difference between λ_0 of sodium hydroxide and the sodium salt of the acid is $192 - 33{\cdot}5 = 158{\cdot}5$. Therefore, if these two electrolytes were equally dissociated, the repression of the hydrolysis would diminish the value of λ by

$$(2{\cdot}24 \times 10^{-3} \times 158{\cdot}5) \times 78{\cdot}8/85 = 0{\cdot}33.$$

Hence $\lambda_{32} = 78{\cdot}47$ and $2\lambda_{32} - \lambda_4 = 84{\cdot}05$.

The graph of λ against $\sqrt[3]{C}$ gives λ_0 as 84—85, and we use 84·5 as the most probable value. Hence the mobility of the anion is 33·5, and λ_0 of the free acid is 380·5. The conductivity of the acid remained constant when the solutions were kept in contact with the electrodes.

	First series.		Second and third series.			
v =	700	1400	288	349	576	1152
λ =	12·5	17·8	7·85	8·5	11·45	15·75
$K \times 10^6$ =	1·65	1·67	1·53	1·48	1·65	1·56

The mean value of K is $1{\cdot}59 \times 10^{-6}$ ($p_K = 5{\cdot}80$), which is only about $\frac{1}{10}$ of that found by Bader ($1{\cdot}29 \times 10^{-5}$).

The preparation showed all the usual criteria of purity, however, and the solutions were made up with the usual precautions.

4-*Nitroresorcinol.*—4-Nitrosoresorcinol, prepared according to Henrich (*Ber.*, 1902, **35**, 4193), was oxidised with alkaline hydrogen peroxide (Borsche and Berkhout, *Annalen*, 1904, **330**, 106). In order to obtain any yield at all, it is essential (*a*) that the hydrogen peroxide should be not weaker than 3%, and (*b*) that the solution should be kept alkaline as long as possible, *i.e.*, after the reaction is over it must be kept boiling for at least ½ hour and concentrated to a convenient bulk, then acidified, and extracted with ether. The product after recrystallisation from hot water is the semihydrate, yellow crystals, m. p. 82°. It may be quickly dehydrated at 70° giving the anhydrous compound, m. p. 115°.

	First series.		Second series.		
v =	69	138	186	372	744
λ =	3·11	4·37	5·56	7·35	11·08
$K \times 10^6$ =	0·98	0·97	1·16	0·99	1·11

The mean value of K is $1{\cdot}04 \times 10^{-6}$ ($p_K = 5{\cdot}98$), which agrees fairly well with Bader's value, $1{\cdot}2 \times 10^{-6}$.

The compound is colourless in acid solution, and completely yellow between p_H 9 and 10. There is no further change in colour in more alkaline solution. The mean value of the first, and only, colorimetric constant is $K_1 = 1{\cdot}55 \times 10^{-9}$, $p_K = 8{\cdot}81$.

Discussion of Results.

It was not expected that the constants of compounds which undergo tautomeric changes would be as uniform as those of normal electrolytes; these changes are probably the cause of the "drifts" which were found in several cases. The irregularities which are found in some cases have been already traced to irreversible or only partly reversible changes brought about by the catalytic activity of the electrodes. The constant of the somewhat similar, although less sensitive, *p*-nitrophenol has been found by Holleman (*Rec.*

trav. chim., 1902, **21**, 432) to vary between 6·1 and 7·3 $\times$ 10^{-8}, while Hantzsch gives 9·6 $\times$ 10^{-8}. We have tested the constants over all available dilutions. In Table I the first dissociation constants are represented by K_e in order to distinguish them from the colorimetric constants—first, $_1K_c$; second, $_2K_c$, and third, $_3K_c$. The compounds have been arranged in each group as far as possible in the order of diminishing first dissociation constants, K_e. Some of these, however, can be regarded as practically identical, in view of the probable errors mentioned above. The mononitrodihydric, like the mononitromonohydric, phenols are about equal in strength, but the dinitro-compounds, like the dinitrophenols, show a considerable difference in this respect. It is, however, in the relation between K_e and the K_c values that both mono- and di-nitro-dihydric phenols show the greatest individuality: so much so that a single conductivity measurement, combined with a colorimetric determination in a solution of known p_H would serve to distinguish each compound quite clearly.

In Table I, the constants of the nitrophenols are given for comparison, the values of K_e being due to Holleman (*loc. cit.*) and those of K_c to Michaelis and Gyemant (*Biochem. Z.*, 1920, **109**, 166). The fourth, fifth, and sixth columns give the constants of the tautomeric changes into the yellow, then the red, and purple forms (if any). The figures in the third column assign each compound to its predominant tautomeric form (Ph. = phenolic; Qu. = quinonoid) and attempt to define its strength as an acid dissociating in this form (K_e').

The experimental constants summarise the equilibria between the tautomeric forms, HM_1 and HM_2, and the products of their dissociation. In the equations, HM_1 stands for the phenolic acid (Ph.), HO·R·NO_2, and HM_2 for the quinonoid or *aci*-form (Qu.), O:R:NO·OH:

$$K_e = \frac{[H^\cdot][M'_1 + M'_2]}{[HM_1 + HM_2]} \quad \text{and} \quad K_c = \frac{[H^\cdot][HM_2 + M'_2]}{[HM_1 + M'_1]} \ *$$

* K_e and K_c are the "apparent" constants, due to the two forms present together, and obtained by electrometric and colorimetric measurements, respectively. Experimental results show that these measurements do in many cases give "mass-action" or Ostwald constants, which do not vary more than those obtained in the case of some of those acids having no tautomeric forms. The expressions for K_e and K_c do not, however, imply constancy unless there are other constants regulating the equilibria between the tautomeric forms, as has been shown by Noyes (*J. Amer. Chem. Soc.*, 1910, **32**, 815; see also Prideaux, "Theory and Use of Indicators," p. 129, Constable, 1917). The drift in the case of some constants may be due to the fact that the equilibria between the tautomeric forms do not obey the law of "mass" or concentration action. We have not yet been able to devise a method of testing this hypothesis.

TABLE I.

Compound.	K_c, as p_K.	K_e', as p_K.	${}_1K_c$, as p_K.	${}_2K_c$, as p_K.	${}_3K_e$ as p_K.
Mononitrophenols.					
2-Nitrophenol	7·17	7·04 (Qu.)	6·05		
4- ,, ...	7·19		7·2		
3- ,, ...	8·0		8·35		
Dinitrophenols.					
2 : 6-Dinitrophenol	3·57		3·70		
2 : 4- ,, ...	4·0		4·06		
2 : 3- ,, ...	4·89				
2 : 5- ,, ...	5·16		5·16		
3 : 4- ,, ...	5·37				
3 : 5- ,, ...	6·68				
Dihydric mononitrophenols.					
3-Nitropyrocatechol	5·73	5·55 (Qu.)	4·95	11·03	High
2-Nitroresorcinol	5·80	5·80 (Qu.)	Low	6·34	—
4- ,, ...	5·98	5·98 (Ph.)	8·81	—	—
2-Nitroquinol	6·00	6·00 (Qu.)	3·25	7·2	10·2
4-Nitropyrocatechol	6·45	6·30 (Qu.)	5·56	10·96	—
Dihydric dinitrophenols.					
2 : 4-Dinitroresorcinol	3·05	3·3 (Ph.)*	3·9 ± 0·4	—	—
3 : 5-Dinitropyrocatechol	3·54	3·14 (Qu.)	3·25	10·3	High
4 : 6-Dinitroresorcinol	3·98	4·60 (Ph.)	4·22	—	—
2 : 6-Dinitroquinol	4·00 ± 0·2	3·3 (Qu.)†	2·8	5·2	9·05

* $\alpha = 0{\cdot}4 \quad 0{\cdot}5 \quad 0{\cdot}7 \qquad p_{K_e}' = 3{\cdot}21 \quad 3{\cdot}24 \quad 3{\cdot}47.$

† $\alpha = 0{\cdot}177 \quad 0{\cdot}211 \quad 0{\cdot}236 \quad 0{\cdot}280 \qquad p_{K_e}' = 2{\cdot}96 \quad 3{\cdot}13 \quad 3{\cdot}43 \quad 3{\cdot}64.$

Thus the constant K_c measures the tendency of the compound to undergo the tautomeric change under the influence of diminishing hydrogen-ion concentration, whether this change takes place in the undissociated molecule or in the ion. The constant K_e contains the molecules and ions which take part in the dissociation of the first hydrogen ion from both the tautomeric forms. Although neither of the two true dissociation constants can be deduced from K_e by a rigid algebraic proof, yet by taking into account numerical relations, on the assumption that the colorimetric constant gives correctly the relative amount of coloured form, $HM_2 + M'_2$, the true dissociation constants of HM_1 or HM_2 may be obtained. The following is an outline of the reasoning and calculations by which these true constants (column 3 in Table I) were derived.

Where K_e is much greater than K_c, it is practically identical with the true dissociation constant of the phenolic acid. On the other hand, where K_e is much less than K_c, it is practically identical with the true constant of the quinonoid acid. Where $K_e = K_c$, the original Ostwald theory of indicators must be used, since ionisation proceeds *pari passu* with tautomeric change. Where K_e and K_c are of the same order, but not too close to one another, the true constants may be calculated as described below. The

limiting ratios of K_e to K_c at which such calculations become necessary will depend on the accuracy with which the original constants are defined by the experimental work.

If $K_e \gtrless 100K_c$, K_e is the constant of the phenolic acid, for even at a degree of ionisation $\alpha = 0{\cdot}8$, the amount of the coloured tautomeride is negligible. In the case of the mononitro-compounds, the degree of ionisation does not exceed 0·05 at the highest dilutions investigated. In the case of the dinitro-compounds, we have not, in determining the constants, taken into account degrees of ionisation exceeding 0·5, since, according to the usual estimate, the secondary ionisation of a dibasic acid may begin to be appreciable at this degree of primary ionisation.

Even at much lower ratios of K_e/K_c, the true constant of the phenolic acid, K'_e, is not far from the observed constant, K_e. The correction of K_e to K'_e will be greatest if all the quinonoid tautomeride is present as ion, and we will make this assumption. The total ion concentration is $M'_1 + M'_2$ and this is equal to $M'_1 + x$, if x is the degree of transformation (of total compound) into M'_2. Suppose that the ratio K_e/K_c is 20, and that the conductivity is determined at a degree of dissociation of 0·25; then

$$(1 - x)/x = [H^+]/K_c \quad . \quad . \quad . \quad . \quad . \quad (1)$$

in which x is the degree of colour change, and

$$(1 - \alpha)/\alpha = [H^+]/K_e \quad . \quad . \quad . \quad . \quad . \quad (2)$$

in which α is the degree of ionisation.

Therefore, on the above assumption,

$$[H^+] = K_e(1 - \alpha)/\alpha = 3K_e \text{ and } x = 1/[1 + 3K_e/K_c) = 1/61$$

Also $$3(M'_1 + 1/61) = (1 - M'_1 - 1/61),$$

therefore $M'_1 = 0{\cdot}233$, and the true constant of HM_1, $K'_e = 0{\cdot}233[H^+]/0{\cdot}75$

or $$K_e' = 0{\cdot}93K_e; \text{ since } K_e = 0{\cdot}25[H^+]/0{\cdot}75.$$

Correction of the Constant of the Phenolic Acids.—When the ratio K_e/K_c is still lower, the observed constant may be corrected for the presence of the ion of the quinonoid form. From the conductivity results we select one or more values of α. Then $p_H = p_{K_e} + \log \alpha/(1 - \alpha)$. By introducing the corresponding value of $[H^+]$ into the equation $\log (1 - x)/x = p_{K_e} - p_H$, the value of x is obtained.

Now since $x = M'_2$, $M'_1 = \alpha - x$, and $HM_1 = 1 - \alpha$,

therefore $$p_{K'_e} = p_H - \log (\alpha - x) + \log (1 - \alpha) \quad . \quad . \quad (3)$$

Correction of the Constants of the Quinonoid Acids.—If K_c is greater than K_e, the observed electrolytic dissociation is mainly that of the

quinonoid form. The most natural assumption, and that which requires the largest correction of the observed constants, is that all the ion consists of M'_2, the remainder of the quinonoid form being present as HM_2. The true constant K'_e of this form can be determined by a simple calculation. Selecting a degree of transformation x (*e.g.*, 0·8), we calculate the corresponding value of $[H^+]$ from equation (1) above. Then substitute this in equation (2), and calculate α and hence also $x - \alpha$ from the equation $\log (1 - \alpha)/\alpha = p_{K_e} - p_H$.

Thus in the case of 3-nitropyrocatechol, when $x = 0{\cdot}8$, $p_H = 5{\cdot}55$, $\alpha = 0{\cdot}402$ at this p_H, and $x - \alpha = 0{\cdot}398$. Hence

$$p_{K'_e} = p_H + \log (x - \alpha)/\alpha = 5{\cdot}54 \quad . \quad . \quad . \quad (4)$$

In calculating α from equation (2) in cases where K_e shows a trend, that value of p_{K_e} is used which corresponds according to the conductivity results to *each* value of α. In these cases, the corrected constant also shows a trend.

Orientation and Polarity.—The orientation of the compounds tabulated can be regarded as exerting influence upon (1) the strengths of the phenolic acids, (2) the strengths of the quinonoid acids, and (3) the colorimetric constants of the tautomeric changes. The two principal aspects of orientation which have received most attention are (*a*) the propinquity of substituting groups, the well-known effects of which have long been systematised without any hypothesis as to mechanism; and (*b*) the alternation of substituting groups, the effect of which is intelligible on the electronic theory of valency.

It should be possible to explain the order of the constants which represent (1), (2), and (3) in a quantitative manner, by the principles (*a*) and (*b*). The residual charges, detected by Lewis's method in the electronic formulæ for $\cdot NO_2$ (Lowry, *Trans. Faraday Soc.*, 1923, **18**, 285), cause it to act as a key radical in maintaining the polarity of a conjugated system. The nitrogen atom, on account of its mixed bond in $\cdot NO_2$ (O=N---→O), assumes a virtual positive charge and confers a virtual negative charge on the carbon atom to which it is attached, and this by alternation of the mean directions in which the electrons oscillate or vibrate, strengthens the virtual negative charges on the carbons in the 3- and 5-positions and weakens those in the 2-, 4-, and 6-positions.

Thus when a hydroxyl group is attached to the 3- or 5-position, weaker phenolic acids should result than when it is attached to the 2-, 4-, or 6-position. There might also be a reciprocal effect of the hydroxyl group on the nitro-group, which will become evident when the ·OH becomes :O. Our results seem to show that the effect of

·NO·OH on :O, and reciprocally, is similar to that of $\cdot NO_2$ on ·OH; so that factors (*a*) and (*b*) act in the same sense on the quinonoid as on the phenolic acids. These effects may first be illustrated by the nitro- and dinitro-phenols.

o-Nitrophenol, in which factors (*a*) and (*b*) are both at a maximum, has a slightly higher constant than *p*-nitrophenol, in which (*b*) is favourable but (*a*) is less so (Holleman, *loc. cit.*). Both are higher in Table I than *m*-nitrophenol, in which (*b*) is unfavourable. The greater tendency to tautomeric change in the *o*- and *p*-compounds is shown by the dissociation of the ortho-compound largely as a quinonoid substance, and of the meta-compound in the phenolic direction. In the case of *p*-nitrophenol, dissociation and tautomeric change are almost parallel.

In the case of the dinitrophenols also, it is remarkable how close the colorimetric lies to the dissociation constant in those cases where both are known. The order of the constants agrees on the whole with the alternate polarity theory. In the strongest, 2 : 6-dinitrophenol, (*a*) and (*b*) are at a maximum; in the 2 : 4-compound (*b*) is favourable and (*a*) not so favourable. In 2 : 3-dinitrophenol, the strengthening effect of the 2-nitro-group is somewhat weakened by the opposing effect of the 3-nitro-group. In the 2 : 5-compound, the opposing effect of the second nitro-group is more marked as the hydroxyl group is exposed to it more directly. In the 3 : 4-, the nitro-group opposing the dissociation is nearer to the hydroxyl than that which favours it. In the 3 : 5-, both nitro-groups alternate incorrectly. It must be noted that the "opposition" of a nitro-group which alternates incorrectly is really only a smaller enhancing effect, since all dinitro-phenols are stronger acids than mononitro-phenols, owing, no doubt, to the more numerous chances for the formation of the quinonoid molecule *whatever* the position of the second nitro-group.

In contrast to the nitrophenols, the nitro-dihydric phenols show the most varied relations between first dissociation and colorimetric constants.

The Mononitro-compounds.—K_c is greater than K_e in the case of 2-nitroquinol, 2-nitroresorcinol, 3- and 4-nitropyrocatechols, 3 : 5-dinitropyrocatechol, and 2 : 6-dinitroquinol, which therefore dissociate chiefly or wholly as quinonoid acids; whilst K_e is greater than K_c in the case of 4-nitro-, and 2 : 4- and 4 : 6-dinitroresorcinol, which therefore dissociate chiefly or wholly as phenolic acids.

The first dissociation constants of the mononitro-compounds are of the order 1×10^{-6}, the constant thus being increased about 10-fold by the introduction of a second hydroxyl group into the molecule of *o*-nitrophenol. The nitro-group is in the ortho-position

to at least one hydroxyl group, *i.e.*, condition (*a*) is favourable, in all the compounds except 4-nitropyrocatechol, which has a distinctly lower constant than the others. One might perhaps expect 3-nitropyrocatechol to be a weaker acid than the 4-nitro-isomeride, instead of *vice versa*. The position of the second hydroxyl group appears, however, to have only a slight effect on the constant. Regarding the first four compounds in this series as derivatives of *o*-nitrophenol, we see that the effect of the second hydroxyl group in decreasing the constant $p_K = 7{\cdot}17$ (*i.e.*, increasing the constant K_c) of *o*-nitrophenol increases in the order 4 = 5, 3, 6. The order of increasingly favourable alternating effect (which agrees with the increase of constant in the order, *o*-, *m*-, and *p*-, in the case of mononitrophenols and some other compounds) is 4, 6, 5, 3. The order of increase in the case of the dihydroxybenzoic acids (with one hydroxyl group ortho to the carboxyl group) is 5, 4, 6, 3 (Lehfeldt, "Electrochemistry," Longmans), which is identical with the order required by condition (*a*) above, *i.e.*, mere propinquity without alternation. The dissociation of the carboxyl group would appear to be more powerfully affected by propinquity, (*a*), and that of the ·NO·OH group by alternation, (*b*), where the two principles are in opposition.

The Dinitro-compounds.—It was considered surprising by Bader (*loc. cit.*), in view of the negative character of hydroxyl, that dinitroquinol should be a weaker acid than 2 : 6-dinitrophenol. This may perhaps be explained as being due to a diminution of the negative polarity of the carbon attached to the ·NO·OH group by the opposing positive polarity of the carbon attached to the 4-hydroxyl group. 2 : 4-Dinitroresorcinol, in which the alternate polarities are in tune, is a stronger acid than 2 : 4- or even than 2 : 6-dinitrophenol.

Comparing the constants of the dinitro- with those of the corresponding mononitro-compounds, there is seen to be an increase in K (decrease in p_K of 1·5—3 units). The polarity of the second nitro-group always enhances that of the first, since the list examined includes only *m*-dinitro-compounds.

The order of the corrected constants is the same as that of the mononitro-compounds from which they are derived :

3-Nitropyrocatechol > 2-nitroresorcinol > 2-nitroquinol = 4-nitroresorcinol *
3 : 5-Dinitropyrocatechol > 2 : 4-dinitroresorcinol = 2 : 6-dinitroquinol > 4 : 6-dinitroresorcinol

* The meta-dinitro-derivative of 4-nitropyrocatechol has not been examined.

The tendency to undergo tautomeric change is measured by the colorimetric constants. The order of these is different from that

of the dissociation constants, and is nearly the same in the dinitro-compounds as in the mononitro-compounds from which they are derived. Thus it is apparently the orientation of one nitro-group in relation to the two hydroxyl groups which determines the number of tautomeric changes and the p_H at which they occur.

Order of $_1K_c$.

* 2-Nitroresorcinol>2-nitroquinol>3-nitropyrocatechol > 4-nitropyrocatechol >4-nitroresorcinol,
2 : 6-Dinitroquinol>3 : 5-dinitropyrocatechol>2 : 4-dinitroresorcinol >4 : 6-dinitroresorcinol †

* The constant is too high to be measured.
† The constant is rather uncertain.

To the second and third colorimetric constants given in our previous communication have now been added all those which can be determined. The nitroresorcinols do not give second constants, with the single exception of the 2-isomeride which undergoes its first change of colour at an exceptionally low p_H, whilst the change of the 4-isomeride occurs at an exceptionally high p_H. The second changes (half-way) to the red or brown forms occur at p_H's from 4 to 6 units lower than the changes (half-way) to the yellow form. The order of the second constants is very similar to that of the first:

$_1K_c$ | 2-N.R.>2 : 6-N.Q.>2-N.Q. = 3 : 5-N.C.>2 : 4-N.R.>3-N.C.> 4-N.C.>4-N.R.
$_2K_c$ | 2 : 6-N.Q.>2-N.R.>2-N.Q.>3 : 5-N.C.>3-N.C. = 4N.C.

The only compounds which undergo the third change, to purple, are nitroquinols and nitropyrocatechols (but not 4-nitropyrocatechol); those in the latter class, however, only show this change in such strong alkali that p_{K_3} could not be determined. The order of the third constants is nearly the same as that of the second:

$_2K_c$ | 2 : 6-N.Q.>2-N.Q.>3 : 5-N.C.>3-N.C. = 4-N.C.
$_3K_c$ | 2 : 6-N.Q.>2-N.Q.>3 : 5-N.C.>3-N.C. —

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CCCVIII.—*The Constitution of the Disaccharides. Part XV. Sucrose.*

By JOHN AVERY, WALTER NORMAN HAWORTH, and EDMUND LANGLEY HIRST.

THE normal variety of *d*-fructose has now been brought within the generalisation that hexoses and pentoses tend to exist ordinarily as amylene-oxide forms (Haworth and Hirst, J., 1926, 1858;

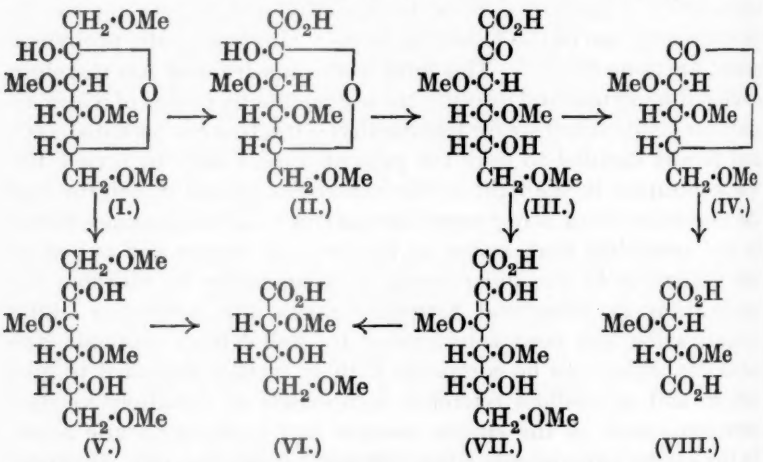
Haworth, Hirst, and Learner, this vol., p. 1040). This development has necessitated the abandonment of the butylene-oxide formula generally current for the normal sugar and latterly supported by the experiments of Irvine and Patterson (J., 1922, **121**, 2696), and has in consequence introduced many uncertainties into the reasoning by which the constitution of the more labile γ-isomeride of fructose was deduced. This consequence was indicated in the papers by two of us referred to above.

It will be seen on reference to the papers by Haworth and Linnell (J., 1923, **123**, 294) and by Haworth and Mitchell (*ibid.*, p. 301) that the inferences drawn from the experimental work therein recorded were based on the appropriation of the butylene-oxide structure for normal fructose. The consideration of a butylene-oxide structure for γ-fructose derivatives was for this reason excluded, the conclusion being drawn that "the choice of a constitution for the tetramethyl γ-fructose derived from methylated sucrose appears to be limited to one of the following forms: ethylene oxide, propylene oxide, amylene oxide." This later work on *n*-fructose has therefore rendered uncertain and insecure the arguments by means of which an amylene-oxide structure for tetramethyl γ-fructose has been deduced, and it was decided to take the present opportunity to review the whole position in the light of the experience gained in determining the constitution of other sugar derivatives. It has become evident in the meantime that, owing to the peculiar nature and extent of the isomerism in the sugar group, it is necessary to withhold the application of structural formulæ unless the substance under investigation has been transformed by well-defined methods into products which can be compared with or further degraded to give simple and crystalline reference compounds of definitely verified structure, such as the simple tartaric and hydroxyglutaric acids. In the earlier experiments (Haworth and Linnell, *loc. cit.*; Haworth and Mitchell, *loc. cit.*) the oxidative degradation products were, with few exceptions, liquid distillates and an extended examination of these substances has now yielded crystalline derivatives of such a nature that the structure of the tetramethyl γ-fructose from which they originated may be clearly deduced.

The experiments now to be described have involved a repetition of the work previously recorded on the oxidation of tetramethyl γ-fructose (I) by nitric acid and by alkaline permanganate, with the result that the accuracy of these experimental data has been substantiated, and proof has been obtained that in almost every case the products described, although liquids, were essentially homogeneous.

Oxidation of tetramethyl γ-fructose with either dilute or concen-

trated nitric acid leads, after esterification with ethyl alcohol, to the isolation of an ethyl ester giving C, 50·4; H, 7·8; OMe, 47·6, which agree reasonably well with either of the formulæ $C_{11}H_{20}O_7$ or $C_8H_{14}O_5$. This ethyl ester reduces Fehling's solution on warming, undergoes profound decomposition in the presence of hot alkali, and contains a reducing hydroxyl group which can be methylated to give a stable, non-reducing substance, the behaviour of which towards alkali is now normal. Owing to this behaviour with alkali, the quantitative hydrolysis of the ethyl ester gave figures which were higher than those calculated for $C_{11}H_{20}O_7$ and agreed with those required by a substance $C_8H_{14}O_5$; but, although the recorded analytical data and the behaviour during titration are in better agreement with the lactone formula $C_8H_{14}O_5$, originally proposed by Haworth and Linnell, yet this compound must now be recognised, for the following reasons, as the ethyl ester, $C_{11}H_{20}O_7$, of the lactol acid $C_9H_{16}O_7$ (II).



On methylation of this product, the higher homologue was obtained which was characterised by its conversion to a crystalline amide, m. p. 99—100°, identical with that previously described by Haworth, Hirst, and Nicholson (this vol., p. 1517). The relationship between the methyl ester obtained by these authors and the ethyl ester now described is thus demonstrated. The degradation of the lactol acid by means of alkaline permanganate yielded a hydroxymethoxy-acid which was isolated in the form of its methyl ester. In the experimental section the detailed analysis of this is described, and it is shown that the main product is occasionally accompanied by an impurity which substantially enhances the methoxyl and titration values. Specimens of the ester gave analytical figures which corresponded closely with those recorded by Haworth and Linnell

for their final esterified oxidation products, whilst others corresponded more nearly to methyl hydroxydimethoxybutyrate.* By treatment with methyl-alcoholic ammonia, each of them gave, in yield varying from 60—87%, the crystalline amide, m. p. 104—105°, of a hydroxydimethoxybutyric acid (VI), proof being thus afforded that the latter acid was the essential constituent. The same product was also obtained by direct oxidation of tetramethyl γ-fructose with alkaline permanganate (compare Haworth and Mitchell, *loc. cit.*), and the identity of the hydroxydimethoxybutyric acid from both these sources was demonstrated by the conversion of each specimen into the same crystalline amide. Methylation of the ester gave a methyl trimethoxybutyrate, which was characterised through the corresponding crystalline amide, m. p. 58—59°.

Under certain conditions, the above hydroxydimethoxybutyric acid appeared to lose the elements of water and give a hygroscopic anhydride, which has been described previously as a lactone by Irvine and Patterson (J., 1922, **121**, 2699) and by Haworth and Mitchell (*loc. cit.*). Sufficient evidence is not yet available, however, to enable a final choice to be made between the formulation of this anhydride as a lactone or a lactide (see footnote).

The application of the Weerman test (*Rec. trav. chim.*, 1917, **36**, 16) as a method for characterising α-hydroxy-acids by the action of sodium hypochlorite on their amides, indicated that the hydroxydimethoxybutyric acid under examination did not belong to this class, and the attempted oxidation of the free acid by means of nitric acid led to the recovery of the material unchanged, thus proving that the free hydroxyl group did not occupy a terminal γ-position in the chain. These indications pointed provisionally to the recognition of the hydroxydimethoxybutyric acid as a β-hydroxy-acid.

A complete verification of these results was secured, and a simple and direct proof of the structure of these substances and of γ-fructose derivatives was attained, by the degradative oxidation of the lactol acid $C_9H_{16}O_7$ (II) by means of barium permanganate in acid solution. Under conditions which required careful control, one

* The reason for this variability of composition becomes clear when it is recognised, as will appear later in this paper, that we were handling a β-hydroxy-acid. The parent substance of this product, β-hydroxybutyric acid, has been fully investigated by McKenzie (J., 1902, **81**, 1402), who has observed the readiness with which it passes into an anhydride form and into crotonic acid by loss of water. If in the present case a dimethoxycrotonic acid were formed, this would lead under the conditions employed to methoxymalonic acid, and ultimately to its methyl ester. We are at present studying the various forms of hydroxydimethoxybutyric acid, obtained synthetically from dimethoxyacetoacetic ester.

atomic proportion of oxygen was absorbed for each molecule of lactol acid, and a yield of nearly 50% of crystalline *d*-trimethyl γ-arabonolactone (IV) was obtained. We were able to recognise this compound with certainty, since we were in possession of the corresponding *l*-isomeride of the lactone (Baker and Haworth, J., 1925, **127**, 365; Haworth and Nicholson, J., 1926, 1899; Drew, Goodyear, and Haworth, this vol., p. 1244), and the properties of the two specimens are given for comparison :

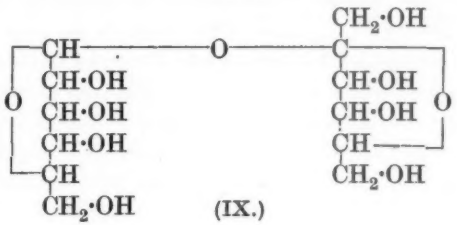
	d-Trimethyl γ-arabonolactone.	*l*-Trimethyl γ-arabonolactone.
M. p.	32—33°	33°
$[\alpha]_D$ (initial) in water.....	+44·5°	−44·2°
$[\alpha]_D$ (after 20 days)	+25·5°	−25·2°

We have confirmed the structure assigned to these lactones, wherein the methyl groups are allocated to the positions 2, 3, 5, by effecting their further oxidation with nitric acid. The *d*-trimethyl γ-arabonolactone originating from tetramethyl γ-fructose gave *l*-dimethoxysuccinic acid (VIII), identified as the crystalline methylamide and also as the amide, and these crystalline derivatives were compared directly with specimens which were specially prepared from *l*-tartaric acid (see later papers by Haworth, Hirst, and Learner and by Haworth and Jones).

The reaction between the lactol acid and acid permanganate is thus typical of the behaviour of either α-ketonic acids or ketol-acids which are potentially α-ketonic in nature (compare Ohle, *Ber.*, 1927, **60**, 1165), leading to the formation of a carboxylic acid containing one carbon atom less in the chain. Since the substance isolated in the present instance has been proved definitely to be 2 : 3 : 5-*d*-trimethyl arabonic acid, it follows immediately that the original lactol acid must have contained methyl groups in positions 3, 4, and 6. The oxide linking present in the lactol acid and also in tetramethyl γ-fructose must connect the carbon atoms in positions 2 and 5. Tetramethyl γ-fructose has therefore a γ- or butylene-oxide structure, and the lactol acid, $C_9H_{16}O_7$, is seen to have the constitution provisionally applied to it by Haworth and Hirst (1926). Similarly the hydroxydimethoxybutyric acid (VI) is recognised as 2 : 4-dimethyl *d*-erythronic acid.

The recent views we have expressed (Haworth, Hirst, and Nicholson, *loc. cit.*) relating to the structure of tetramethyl γ-fructose, resting on the analogy with other γ-sugars and on the ease of transformation of γ-fructose derivatives into furan bodies (see also Bergmann, J., 1923, **123**, 1277), are thus finally supported by the experimental results herein outlined. It follows that this sugar is now to be recognised as 1 : 3 : 4 : 6-tetramethyl fructose, and since

this derivative arises from the hydrolysis of methylated sucrose, the constitutional formula (IX), which we have applied in recent papers to sucrose, receives additional support and confirmation.



(IX.)

EXPERIMENTAL.

Oxidation of Tetramethyl γ-Fructose with Nitric Acid (d 1·42). *Isolation of the Ethyl Ester of the Lactol Acid* $C_9H_{16}O_7$ (II).—A mixture of tetramethyl γ-fructose (10 g.) and concentrated nitric acid (70 c.c.; *d* 1·42) was cautiously heated on the water-bath until at 70° a vigorous reaction ensued with evolution of nitrous fumes. The reaction was kept under control by cooling at intervals, and the temperature of the mixture was gradually raised to 93°. The reaction appeared to be complete after 1½ hours. Water was then added to the cooled solution and the nitric acid was almost entirely removed by distillation at 50—60°/13 mm., the usual precautions being observed to avoid undue heating during the concentration. This procedure was many times repeated and finally the product was taken down to a syrup. At this stage, absolute ethyl alcohol was added and distilled from the product to remove water. The syrupy residue was dissolved in 200 c.c. of absolute ethyl alcohol, containing 6 g. of hydrogen chloride, and boiled gently under reflux for 9 hours. Thereafter, the mineral acid was neutralised with silver carbonate, the solution filtered, and the solvent evaporated. The syrupy residue distilled without decomposition:

Fraction 1, at bath temperature up to 125°/0·1 mm.; 2·2 g., $n_D^{16°}$ 1·4500.

Fraction 2, at bath temperature 130—135°/0·1 mm.; 7 g., $n_D^{14°}$ 1·4520.

Fraction 3, at bath temperature 150°/0·1 mm.; 0·5 g., $n_D^{14°}$ 1·4564. Fraction 2, which showed $[\alpha]_D^{24°}$ + 25·8° in water (c = 2·7), gave the following analytical data—Found: C, 50·35; H, 7·75; OMe, 47·6. $C_{11}H_{20}O_7$ requires C, 50·0; H, 7·6; OMe, 47·0. $C_8H_{14}O_5$ requires C, 50·5; H, 7·4; OMe, 48·9%. This material reduced Fehling's solution on warming and gave coloured decomposition products when heated with aqueous alkali. As stated on p. 2310, this product consisted essentially of the ethyl ester, $C_{11}H_{20}O_7$, of the

lactol acid, $C_9H_{16}O_7$ (II). *Titration.* 0·269 G. required 13·5 c.c. *N*/10-sodium hydroxide (on heating for ½ hour at 90°). Calc., for $C_{11}H_{20}O_7$: 10·2 c.c.; for the lactone, $C_8H_{14}O_5$: 14·2 c.c.

Methylation and Amide Formation.—A specimen of the above product (Fraction 2) was treated with Purdie's reagents for 5½ hours. A syrup which remained colourless when heated with aqueous alkali and which did not reduce Fehling's solution was obtained, distilling at 12 mm. from a bath heated at 155—160°. This showed $[\alpha]_D^{22°} + 3°$ in water ($c = 1·07$). *Titration.* 0·1048 G. required 4·2 c.c. *N*/10-sodium hydroxide for hydrolysis and neutralisation.

The methylated product was dissolved in methyl alcohol, saturated with dry ammonia, and cooled in ice, and the mixture was kept for 4 days. Removal of the solvent in a vacuum gave a crystalline product (yield above 60%), m. p. 99—100° (from light petroleum); $[\alpha]_{5461}^{21°} - 83°$ in water ($c = 0·98$). A specimen of the crystalline amide was mixed with the specimen of the amide $C_{10}H_{19}O_6N$, obtained by Haworth, Hirst, and Nicholson (this vol., p. 1517) from the corresponding methyl ester, and the m. p. showed no depression.

Oxidation with Alkaline Permanganate.—The product (2·5 g.) isolated from the process of oxidation with nitric acid as described above (Fraction 2) was treated at 70° with 2*N*-potassium hydroxide (20 c.c.) and with *N*-potassium permanganate (88 c.c.), the latter being gradually added with frequent shaking. In working up the product the alkali was neutralised with mineral acid in presence of ice, and after removal of the precipitated manganese oxides the filtrate was made slightly alkaline by means of potassium carbonate and evaporated (water-bath) to small bulk. Thereafter the whole of the water was removed in a high vacuum, yielding a white, solid mass. Preliminary experiments showed that no advantage was to be gained by extracting the solid with organic solvents. It was therefore dissolved in water and the organic acid liberated by acidifying with mineral acid. The water was then removed in a high vacuum, and the white mass extracted with chloroform. This extract yielded a syrupy organic acid which was esterified with methyl-alcoholic hydrogen chloride. The liquid ester distilled under 0·07 mm. from a bath heated to 100°, and showed $[\alpha]_D^{20°} + 19°$ (in water, $c = 0·96$) and $n_D^{17°}$ 1·4400; yield 0·8 g. (Found : C, 46·3; H, 7·9; OMe, 49·2. $C_7H_{14}O_5$ requires C, 47·2; H, 7·9; OMe, 52·2%). *Titration.* 0·0946 G. required 5·2 c.c. *N*/10-sodium hydroxide for hydrolysis and neutralisation (Calc. for $C_7H_{14}O_5$: 5·3 c.c.).

This product has been obtained on several occasions under similar experimental conditions to those outlined above, and the

physical properties and analyses of these specimens are tabulated below :

(*a*) $n_D^{17^\circ}$ 1·4400, $[\alpha]^{20^\circ}$ + 19°, C, 46·3; H, 7·9; OMe, 49·2%; (*b*) $n_D^{16^\circ}$ 1·4410, $[\alpha]_D^{19^\circ}$ + 22·4°, OMe, 54·9%; (*c*) $n_D^{13\cdot5^\circ}$ 1·4390, OMe, 48·8%; (*d*) $[\alpha]_D^{20^\circ}$ + 21·8°, C, 46·75; H, 7·8; OMe, 61·2%; (*e*) n_D 1·4421, $[\alpha]_D$ + 31°, C, 47·8; H, 7·2; OMe, 60%.

The analyses of (*a*) and (*d*) were made independently by Fein-Chemie, G.m.b.H., Tübingen. These products correspond with that obtained by Haworth and Linnell (*loc. cit.*, p. 301), who quote C, 48·4; H, 7·2; OMe, 59·7%. It was evident that all these products were mixtures containing a variable quantity of a substance giving high methoxyl and titration values, and this factor is referred to in the footnote on p. 2311. That each of these specimens was essentially, however, methyl hydroxydimethoxybutyrate was demonstrated by treating them with methyl-alcoholic ammonia. This led to the isolation of the crystalline amide described below in yields from 60—87%, the largest yield being obtained from the specimen (*a*).

Hydroxydimethoxybutyramide was isolated as described above as crystals, m. p. 104—105° (from petroleum); $[\alpha]_{5461}^{19^\circ}$ + 37° in water ($c = 1·05$), and $[\alpha]_D^{19^\circ}$ + 33° [Found: C, 44·2; H, 8·0; N, 8·7; OMe, 36·2. $C_4H_7O_2N(OMe)_2$ requires C, 44·2; H, 8·0; N, 8·6; OMe, 38·0%].

Oxidation of Tetramethyl γ-Fructose with Alkaline Permanganate.—In general the method described by Haworth and Mitchell (J., 1923, 123, 306) was followed, except that the product was isolated as the methyl ester as described in the earlier paragraph above. The ester distilled from a bath heated to 130° under 13 mm., and showed $n_D^{14^\circ}$ 1·4413. This material corresponded exactly with the specimens (*a*)—(*e*) described above, and gave on treatment with methyl-alcoholic ammonia a crystalline amide, m. p. 104—105°, identical in all respects with that described above as hydroxydimethoxybutyramide.

Hydrolysis.—A specimen of the above methyl ester was hydrolysed with dilute hydrochloric acid (5%) during 4½ hours at 80°. After the usual process of isolation, the product was distilled from a bath heated to 125° under 0·04 mm., and was obtained as a colourless, hygroscopic syrup having acid properties, but which did not crystallise on preserving in a vacuum over phosphoric oxide for several days. A further purification was effected by fractional distillation, and the substance remained as a colourless syrup. This appeared to be identical with the product obtained by Haworth and Mitchell (*loc. cit.*) and Irvine and Patterson (*loc. cit.*, p. 2699), and described as the lactone of hydroxydimethoxybutyric acid.

The observations now to be recorded indicate, however, that the product may have been a lactide of a β-hydroxy-acid.

Experiments on the Determination of the Structure of the Hydroxydimethoxybutyric Acid.—(a) *Weerman reaction on the amide.* Weerman's method (*loc. cit.*) for the characterisation of α-hydroxy-acids depends on the interaction of the amides of these acids with sodium hypochlorite, this reagent forming sodium *iso*cyanate with such amides but not with those of other hydroxy-acids. The qualitative test applied for the presence of sodium *iso*cyanate is the addition of hydrazine hydrate, followed by the addition of benzaldehyde, which leads to the isolation of benzalsemicarbazone. An alternative method is the addition of semicarbazide, which in presence of sodium *iso*cyanate forms crystalline hydrazidicarbonamide. When the test was applied to the hydroxydimethoxybutyramide which we had prepared during the present work, a negative result was obtained, indicating that this amide was other than an α-hydroxy-compound. Control experiments were carried out with gluconamide, trimethoxyglutaramide and acetamide, and only in the case of gluconamide was a positive result obtained, as should be the case.

(b) *Attempted oxidation with nitric acid.* The above result indicated that the related acid must be either a β- or a γ-hydroxy-acid. In the latter case the hydroxyl group would be in the terminal position as a $-CH_2 \cdot OH$ group, which should be characterised by its ease of oxidation to a carboxyl group. When the substance was digested, however, with nitric acid (*d* 1·2) during 6 hours at 70—100°, it gave a product which, on conversion into the methyl ester, was identical with the original material, thus proving that no oxidation had taken place. This conclusion was verified by conversion of this ester into the crystalline hydroxydimethoxybutyramide, m. p. 104—105°. It became evident, on the basis of these results, that the hydroxydimethoxybutyric acid under examination was probably a β-hydroxy-acid.

(c) *Methylation of the ester.* The specimen (*a*) described previously, and consisting essentially of methyl hydroxydimethoxybutyrate, was methylated with Purdie's reagents, and the product on distillation showed $n_D^{12°}$ 1·4282; $[\alpha]_D^{21°}$ + 19° in water (c = 1·04). *Titration.* 0·1006 G. required 5·25 c.c. of N/10-sodium hydroxide for hydrolysis and neutralisation (Calc. for $C_8H_{16}O_5$: 5·24 c.c.). Found: C, 49·7; H, 6·5; OMe, 62·3. Calc.: C, 50·0; H, 8·3; OMe, 64·6%.

This product was identified as methyl trimethoxybutyrate by conversion into the crystalline amide. The trimethoxybutyramide separated from light petroleum as colourless needles, m. p. 58—59°,

$[\alpha]_D^{18°}$ + 40·5° in water (c = 1·09 (Found: C, 47·7; H, 8·5; N, 7·7; OMe, 49·7. Calc.: C, 47·5; H, 8·5; N, 7·9; OMe, 52·5%).

Confirmatory Proof of the Constitution of Tetramethyl γ-Fructose. Isolation of Crystalline d-2 : 3 : 5-*Trimethyl Arabonolactone by Degradative Oxidation of the Lactol Acid*, $C_9H_{16}O_7$.—The ethyl ester, $C_{11}H_{20}O_7$, of a lactol acid, $C_9H_{16}O_7$, was described as Fraction 2 on p. 2313. Preliminary experiments showed that the desired stage of oxidation by means of acidified permanganate was completed when one atomic proportion of oxygen had been absorbed. The details of the procedure are as follows: The material of Fraction 2 (3·2 g.) was hydrolysed during 3 hours at 90° with 60 c.c. of 2·5% hydrochloric acid. The solution was neutralised with silver carbonate, and the silver removed from the filtrate with the aid of hydrogen sulphide. The filtrate from the silver sulphide was evaporated, and the free lactol acid, $C_9H_{16}O_7$, was collected as a syrup, which was dissolved in 110 c.c. of water and mixed with 40 c.c. of *N*-sulphuric acid. Thereafter, a solution of barium permanganate (4%) was added very slowly until the required amount had been admitted, the reaction being conducted at room temperature. An excess of barium hydroxide solution was then added, followed by the admission of carbon dioxide to precipitate the excess of barium hydroxide. At this stage, the precipitated salts were removed by filtration, and to the solution, which contained the soluble barium salt of an organic acid, the equivalent of dilute sulphuric acid was added. The filtrate obtained after removal of barium sulphate was now evaporated under diminished pressure, and yielded a syrup which crystallised spontaneously when cold (yield 1 g.). The crystalline compound distilled under 11 mm. from a bath at 145°, and the distillate solidified instantly (yield 0·75 g.).

Extraction of this crystalline product with light petroleum left a minute quantity of residual oil which darkened in the air. From the solution in light petroleum, needles or shining plates crystallised according to the conditions of cooling (m. p. 32—33°; yield 0·6 g.); $[\alpha]_D$ + 44·5° in water (c = 0·712)—this initial value decreased during 18 days to the constant value + 25·5° (Found: C, 50·2; H, 7·7; OMe, 47·6. Calc. for $C_8H_{14}O_5$: C, 50·5; H, 7·4; OMe, 48·9%). *Titration.* 0·0512 G. required 2·7 c.c. *N*/10-sodium hydroxide for neutralisation, the substance behaving during titration as a lactone.

This product corresponds to *d*-trimethyl γ-arabonolactone, and in the theoretical section it is shown that the rotation values are equal and opposite to those of the *l*-isomeride, whilst the m. p. is identical.

A similar oxidation was carried out with the corresponding methyl

ester of the lactol acid, $C_{10}H_{18}O_7$ (compare Haworth, Hirst, and Nicholson, *loc. cit.*). In this example, the experiment was modified by omitting isolation of the free acid, inasmuch as control experiments indicated that the alcohol liberated on hydrolysis of the ester was not appreciably oxidised under the experimental conditions employed. The methyl ester (8·9 g.) was heated for 2½ hours at 85° with *N*/2-sulphuric acid (104 c.c.). Barium permanganate equivalent to one atomic proportion of oxygen was then admitted to the cold solution, which had been diluted to a volume of 500 c.c. by the addition of a further 100 c.c. of *N*/2-sulphuric acid and water. The product was isolated in the manner already described, and weighed 4·1 g., of which 3·0 g. were collected as a distillate under 11 mm. from a bath at 145°. This distillate crystallised immediately when cold. A similar portion of an oily by-product was again noticed. The recrystallised *d*-trimethyl γ-arabonolactone, m. p. 33°, weighed 2·6 g.

It should be added that qualitative tests conducted with the ethyl or methyl esters dissolved in acidified permanganate solution showed that the reaction proceeded slowly until hydrolysis of the ester had taken place. Oxidation then proceeded rapidly at room temperature. The oxidation proceeds smoothly and is accompanied by practically no change in the rotation value of the solution.

We wish to thank the Education Committee of the Durham County Council for the award of a Research Exhibition to one of us (J. A.).

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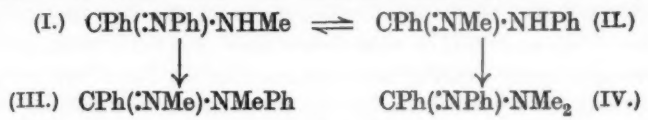
CCCIX.—*The Tautomerism of Amidines. Part VII. Methylation of Benzenyl-*p*-nitrodiphenylamidine.*

By CLIFFORD CHEW and FRANK LEE PYMAN.

THE alkylation by alkyl salts of open-chain amidines, in which one of the nitrogen atoms is attached to an aryl group and the other to a non-aryl (hydrogen or alkyl) group, yields as main products compounds alkylated on the arylamine nitrogen atom, together with small quantities of the isomeric alkyl derivatives. For example, benzenylphenylmethylamidine (I or II) gives with methyl iodide methylphenylamidobenzenylmethylimidine (III) in 62% yield, and dimethylamidobenzenylphenylimidine (IV) in 4% yield (Pyman, J., 1923, **123**, 367).

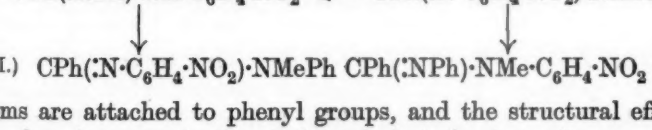
In previous papers (Pyman, J., 1923, **123**, 3359; Forsyth and Pyman, J., 1926, 2502) one of us has expressed the view that results

of this kind are due, not to the feebler basicity of the arylamino-group as compared with the alkylamino-group, as some previous



investigators have supposed, but to the tendency of the aryl group to attract the double linking into the αβ-position. Thus, it was thought that benzenylphenylmethylamidine reacted in the form (I) to a much greater extent than in the form (II), owing to the influence of the phenyl group in the anilino-residue, and consequently gave (III) to a much greater extent than (IV), since the alkylation of open-chain amidines with alkyl salts leads to the attachment of the alkyl group to the nitrogen atom which is doubly linked to carbon (Pyman, J., 1923, **123**, 3359). Evidence that the structural effect is of greater importance than the relative basicities of the nitrogen atoms has been given in the papers quoted, and further evidence in favour of this view is afforded by the results of the present investigation.

Benzenyl-p-*nitrodiphenylamidine* (V or VI) gave on methylation with methyl iodide *benzenylmethylphenylamido*-p-*nitrophenylimidine* (VII) in 28·8% yield, and *benzenylmethyl*-p-*nitrophenylamidophenylimidine* (VIII) in 24·9% yield, together with 8·8% of unchanged material. Now, in benzenyl-*p*-nitrodiphenylamidine both nitrogen



atoms are attached to phenyl groups, and the structural effect of the phenyl groups is thus balanced, but the two nitrogen atoms, which are present as anilino- and *p*-nitroanilino-residues respectively, differ considerably in basicity, for aniline has $K = 4{\cdot}6 \times 10^{-10}$ and *p*-nitroaniline $K = 1 \times 10^{-12}$. The results of the methylation thus show that the marked disparity between the yields of the two methyl derivatives, which is always observed when arylamine and alkylamine residues are in competition for a methyl group, has disappeared here on the elimination of the structural effect of a phenyl group attached to only one of the nitrogens, in spite of a considerable difference between the basicities of the two amino-residues. Further, it is noteworthy that the isomeride isolated in rather larger quantity is that in which the methyl group has become attached to the more basic nitrogen atom. This agrees with the results of alkylating open-chain amidines such

as benzenylmethylamidine, $NMe{:}CPh{\cdot}NH_2 \rightleftharpoons NHMe{\cdot}CPh{:}NH$, in which neither of the nitrogen atoms is attached to a phenyl group (Pyman, *loc. cit.*). The constitutions of the two methylated amidines (VII) and (VIII) were determined by synthesising them from the appropriate methylated amines, and in the course of this work various known methods for the preparation of amidines have been compared, and are referred to below.

Experimental.

Benzenyl-*p*-nitrodiphenylamidine was prepared by several of the available methods.

A. After Gerhardt (*Annalen*, 1858, **108**, 214). Benzanilide-iminochloride (53 g.) and *p*-nitroaniline (33 g.) in dry ether (1 l.) were kept for 4 days. The deposit (22 g.; m. p. 165—195°) was dissolved in hot alcohol (300 c.c.) and kept; the crystals (7·5 g.; m. p. 245—250°) which separated were dissolved in hot alcohol (150 c.c), and when the solution was basified with ammonia, the amidine separated (5·5 g.; m. p. 183°; yield 7%).

B. After Sen and Rây (J., 1926, 646). Benzanilide (10 g.), *p*-nitroaniline (7 g.), and phosphorus trichloride (170 g.) were heated under reflux for 4 hours in an oil-bath at 120—130°, and the amidine was isolated in 15% yield (2·38 g.; m. p. 180—182°).

C. After Hill and Rabinowitz (*J. Amer. Chem. Soc.*, 1926, **48**, 732). Benzanilide (10 g.), *p*-nitroaniline (7 g.), phosphorus trichloride (7 g.), and sodium-dried benzene (44 c.c.) were heated for 5 hours at 100°; the amidine was obtained in 8% yield (1·33 g.; m. p. 182°).

D. After Hill and Cox (*ibid.*, p. 3214). This proved to be by far the best method. To a well-cooled suspension of phosphorus pentachloride (11 g.) in sodium-dried benzene (50 c.c.), benzanilide (10 g.) was added, followed by *p*-nitroaniline (7 g.), and the mixture heated under reflux for 3 hours on the water-bath. The solvent was distilled off, the residue was well ground with aqueous ammonia, and the paste filtered. The precipitate was thoroughly extracted by grinding with cold alcohol and water, and the residue was crystallised from alcohol, the amidine being isolated in 61% yield (9·1 g. of m. p. 182—183° + 0·75 g. of m. p. 179—180°). In a repetition of this experiment with 40 g. of benzanilide, the amidine was isolated in 75% yield (48·7 g.; m. p. 182°).

Benzenyl-p-*nitrodiphenylamidine* (V or VI) crystallises from alcohol in long, lemon-yellow needles, m. p. 184° (corr.) (Found : C, 71·8; H, 5·1. $C_{19}H_{15}O_2N_3$ requires C, 71·9; H, 4·5%). It is insoluble in hot or cold water or in chloroform, but moderately soluble in hot alcohol or ether. On grinding the base with concentrated

hydrochloric acid, a colourless, crystalline *hydrochloride*, m. p. 261°, is obtained, from which the amidine can be regenerated by treatment with ammonia. This hydrochloride is very sparingly soluble in hot water, and when boiled with alcohol containing hydrochloric acid yields *p*-nitrobenzanilide (m. p. crude, 194°; purified, 199°; mixed with a known specimen of m. p. 200°, 200°). In an attempt to prepare a picrate from the amidine and picric acid in hot alcohol, *p*-nitrobenzanilide was again deposited.

Benzenylmethylphenylamido-p-*nitrophenylimidine* (VII).—*p*-Nitrobenzanilide-iminochloride (9 g.), which had been completely freed from hydrogen chloride by keeping in an evacuated desiccator over sodium hydroxide, and monomethylaniline (3·5 g.) in dry ethereal solution were kept over-night, and the solvent distilled. The residue was extracted with hot 2% hydrochloric acid (250 c.c.), which left crude *p*-nitrobenzanilide undissolved (7·2 g.; m. p. 190°; mixed m. p. with a known specimen, 195°). The extract deposited a further 0·26 g. of the same compound on cooling, and the filtrate from this was basified and extracted with ether. The ether residue (3·65 g.) was separated by means of light petroleum into monomethylaniline (1·18 g.; b. p. 193°) and crude amidine (2·3 g.; m. p. 120—128°; yield 19%). It is essential to free the iminochloride from hydrogen chloride before attempting the condensation with monomethylaniline, for otherwise the amidine is not formed. Consequently, it is not surprising to find that this amidine cannot be prepared by the method of Hill and Cox.

Benzenylmethylphenylamido-p-*nitrophenylimidine* crystallises from alcohol in pale yellow plates, which in thin layers have a silvery lustre, m. p. 138° (corr.) (Found: C, 72·5; H, 5·4; N, 12·8. $C_{20}H_{17}O_2N_3$ requires C, 72·5; H, 5·1; N, 12·6%). It is insoluble in hot or cold water, chloroform, or benzene, moderately soluble in cold alcohol, and readily soluble in ether or hot alcohol. The *picrate* separates from alcohol in yellow plates, m. p. 206° (corr.). It is almost insoluble in water or cold alcohol, and explodes when heated in a flame. The *hydrochloride* and *hydriodide* separated from water as gums which could not be crystallised.

Benzenylmethyl-p-*nitrophenylamidophenylimidine* (VIII) could not be isolated from the products of interaction of benzanilideiminochloride (free from hydrogen chloride) with *p*-nitromonomethylaniline in cold or hot dry ether, but was readily prepared by the method of Hill and Cox. Benzanilide (5 g.) was added to a well-cooled suspension of phosphorus pentachloride (5·5 g.) in sodium-dried benzene (25 c.c.). After thorough shaking, *p*-nitromonomethylaniline (3·8 g.) was added, and the mixture heated under reflux for 3 hours on a steam-bath. The solvent was distilled off, and the

residue extracted several times with hot water (1 l. in all), which left very crude benzanilide (0·85 g.; m. p. 140°) undissolved. On being cooled, the extract deposited a yellow product (2·25 g.; m. p. 140—170°) which gave on crystallisation from alcohol the amidine hydrochloride (0·75 g.; m. p. 218—220°), the mother-liquors containing *p*-nitromonomethylaniline. The filtrate from the yellow product was basified with ammonia and extracted with ether, which removed an orange syrup (5·25 g.). This was mixed with concentrated hydrochloric acid and a little alcohol, and filtered from more amidine hydrochloride (3·8 g.; m. p. 216—219°). A further small quantity of this was obtained from the filtrate, and all crops were combined and crystallised from alcohol, 2·78 g. of the pure salt being obtained (yield, 29%).

Benzenylmethyl-*p*-nitrophenylamidophenylimidine was obtained as a pale yellow syrup, which did not crystallise. It is insoluble in cold or hot water or in chloroform, but readily soluble in alcohol or ether. It yields well-crystallised salts. The *hydrochloride* crystallises from alcohol in colourless, rhombic prisms, containing 1EtOH which is not lost at 100°, and melts and effervesces at 226° (corr.) (Found: C, 64·0; H, 5·9. $C_{20}H_{17}O_2N_3,C_2H_6O,HCl$ requires C, 63·9; H, 5·8%). It is sparingly soluble in cold water, moderately soluble in cold alcohol, and very readily soluble in hot alcohol. The *hydriodide* crystallises from alcohol in pale yellow, anhydrous, rhombic prisms, m. p. 225° (corr.) (Found: C, 52·3; H, 4·5. $C_{20}H_{17}O_2N_3,HI$ requires C, 52·3; H, 3·9%). It is very sparingly soluble in cold water, alcohol, or acetone, but readily soluble in hot alcohol or acetone. The *picrate* crystallises from alcohol in yellow needles, m. p. 194° (corr.). It is sparingly soluble in hot water or cold alcohol, but readily soluble in hot alcohol.

*Methylation of Benzenyl-*p*-nitrodiphenylamidine by Methyl Iodide.*—Benzenyl-*p*-nitrodiphenylamidine (35 g.) and methyl iodide (35 c.c.) were heated under pressure for 3 hours at 100°. The partly crystalline product was mixed with acetone, and crude benzenylmethyl-*p*-nitrophenylamidophenylimidine hydriodide (13·8 g.; m. p. 220°) was collected. The filtrate was concentrated, basified with ammonia, and extracted with ether. The ether residue (27·3 g.) was crystallised from alcohol (220 c.c.), which deposited benzenylmethylphenylamido-*p*-nitrophenylimidine (10·2 g.; m. p. 136°) on keeping for 1 hour, whilst the filtrate deposited crude benzenyl-*p*-nitrodiphenylamidine (4·1 g.; m. p. 163°) on keeping over-night. The final mother-liquor was evaporated to a syrup and mixed with concentrated hydrochloric acid (10 c.c.) and a little acetone, whereupon benzenyl-*p*-nitrodiphenylamidine hydrochloride (0·43 g.; m. p. 249°) separated. The filtrate from this was deprived of acetone,

dissolved in dilute hydrochloric acid, and mixed with sodium iodide, crude benzenylmethyl-*p*-nitrophenylamidophenylimidine hydriodide (0·71 g.; m. p. 197°) being then deposited. The filtrate was basified and extracted with ether, which gave a semi-solid residue (10·3 g.). This was crystallised from alcohol and gave crude *p*-nitromonomethylaniline (0·82 g.; m. p. 150°), but no other crystalline material could be isolated from the filtrate. When the various crude products were purified by the methods described earlier in this paper, benzenylmethyl-*p*-nitrophenylamidophenylimidine hydriodide was obtained in 24·9% yield (11·36 g. of m. p. 225° + 0·76 g. of m. p. 224°), benzenylmethylphenylamido-*p*-nitrophenylimidine in 28·8% yield (9·71 g. of m. p. 138° + 0·37 g. of m. p. 137°), and benzenyl-*p*-nitrodiphenylamidine was recovered unchanged in 8·8% yield (2·67 g. of m. p. 181° + 0·41 g. of m. p. 178°).

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CCCX.—*Low-temperature Oxidation at Charcoal Surfaces. Part IV. The Active Areas for Different Acids and their Relative Rates of Oxidation.*

By WINIFRED MARY WRIGHT.

IN previous communications (J., 1925, **127**, 1347; 1926, 1813, 3182), it was demonstrated that the surfaces of charcoals containing both iron and nitrogen could be differentiated by the method of selective poisoning into areas of different catalytic activities for the oxidation of oxalic acid. Whilst it was shown that these areas were differentiated in respect of their structure (the Fe–C–N, Fe–C, and C–C areas), of the rates of oxidation, and of the temperature coefficients of the oxidation processes on the areas, the method of estimating the total active carbon area from the amount of amyl alcohol absorbed only gave a maximum value for the fraction of the surface which was active. It is unlikely that the amyl alcohol is adsorbed preferentially only on the most active area if this is already covered with oxalic acid. It is also improbable that one amyl alcohol molecule is attached to but one carbon atom of the underlying surface. Since the active carbon area, even in very active promoted charcoals, greatly exceeds the more active areas

of the promoted iron and iron–nitrogen patches, it was suggested by Dr. E. K. Rideal that it might be possible to determine both the adsorption of the poison and the displacement of the acid effected on this area.

Two specimens of charcoal were employed, Merck's blood- and Kahlbaum's sugar-charcoal; each charcoal was powdered to pass an 80-mesh sieve and heated for 2 hours at a low red heat in silica crucibles before use. The amyl alcohol content of the aqueous oxalic acid–amyl alcohol solutions employed was determined by the drop-weight method, and the oxalic acid content by titration with permanganate as previously described. The results obtained are shown in Table I.

TABLE I.

A. Merck's Blood-charcoal.

Oxalic acid.			Amyl alcohol.		
Bulk concentration (g.-mol. per l.).	Adsorbed (g.-mol. per g. of C.).	Displaced (g.-mol. per g.).	Bulk concentration (g.-mol. per l.).	Adsorbed (g.-mol. per g. of C.).	Mols. of alcohol required to displace 1 mol. oxalic acid.
0·025	$6{\cdot}93\times10^{-4}$	0	0	0	0
„	$5{\cdot}76$ „	$1{\cdot}17\times10^{-4}$	0·0156	$7{\cdot}31\times10^{-4}$	6·3
„	$4{\cdot}58$ „	$2{\cdot}35$ „	0·0313	$14{\cdot}35$ „	6·1
„	$2{\cdot}20$ „	$4{\cdot}73$ „	0·0625	$26{\cdot}5$ „	5·5
„	0·0 „	$6{\cdot}93$ „	0·125	$49{\cdot}0$ „	(7·1)
0·5	$42{\cdot}0\times10^{-4}$	0	0	0	0
„	$38{\cdot}3$ „	$3{\cdot}7$ „	0·05	$24{\cdot}5$ „	6·6
„	$34{\cdot}0$ „	$8{\cdot}0$ „	0·15	$48{\cdot}3$ „	6·0
„	$30{\cdot}1$ „	$11{\cdot}9$ „	0·25	$69{\cdot}5$ „	5·8
0·75	50·0 „	0	0	0	0
„	36·0 „	14·0 „	0·25	67·0 „	4·8

B. Kahlbaum's Sugar-charcoal.*

0·75	$36{\cdot}9\times10^{-4}$	0	0	0	0
„	$33{\cdot}9$ „	$3{\cdot}0\times10^{-4}$	0·05	10×10^{-4}	3·3
„	$27{\cdot}4$ „	$9{\cdot}5$ „	0·15	26 „	2·7
„	$14{\cdot}9$ „	$22{\cdot}0$ „	0·25	40 „	1·8

* This was a hard brittle charcoal (unlike the soft charcoal used in Part I of this series).

It is clear from these data that the amyl alcohol is by no means preferentially adsorbed in the presence of oxalic acid, but that the number of mols. of amyl alcohol required to desorb one mol. of oxalic acid depends both on the relative concentrations of the two adsorbents and on the nature of the adsorbate. Since with blood-charcoal, at the concentration (0·025*M*) giving the maximum oxidation velocity, 6 mols. of the alcohol only displace 1 mol. of the acid, the adsorption of the former does not give a trustworthy means of estimating the active area.

A search for a more efficient poison was made. Saturated solutions of diphenyl ether, *tert.*-butyl *p*-aminobenzoate, allyl *p*-aminobenzoate, octadecyl acetate, and hexadecylcarbamide were tried, but none of these reduced the rate of oxidation of oxalic acid by more than 70%. Solutions of dibromoacetic acid, ethylene dibromide, saponin, and sodium palmitate were also used; of these the soap was most efficient, giving 75% poisoning, but owing to its colloidal nature it was unsuitable for estimating the active areas. Ethylene dibromide, though very slightly soluble, gave 50% poisoning. A saturated solution of ethylene dibromide in aqueous ethyl alcohol (4% alcohol) gave 93% poisoning with oxalic acid, but further addition of alcohol gave an increased oxygen-uptake, owing to some secondary effect. A few determinations of displacement of oxalic acid by this substance were made, and from the degree of poisoning the active areas were calculated, but these results are untrustworthy owing to the unknown effect of alcohol on the oxidation velocity.

An attempt was made to poison the charcoal for the oxidation of *M*-formic acid by the addition of salts. Silver nitrate, copper sulphate, and aluminium chloride in *N*/100- and *N*/10-solutions were tried, but none of these gave more than 15% poisoning.

Finally, a saturated solution of caproic acid (0·046*N*) was found to be a fairly effective poison of the charcoal for the acids investigated. Its absorption was determined by the drop-weight method.

The results of poisoning Kahlbaum's sugar-charcoal with caproic acid for the oxidation of four acids are given in Table II. [Contrary to our previous results (Part I, p. 1353), we find that formic acid is readily oxidised in the absence of impurities.]

Caproic acid is clearly a more selective poison than any material hitherto examined. We note that 2 mols. of both aminoacetic acid and formic acid, 1·5 mols. of malonic acid, and 1 mol. of oxalic acid are displaced on the adsorption of 1 mol. of caproic acid, from which we may deduce the relative areas of these molecules on adsorption. These small values are somewhat surprising, if, as is frequently assumed to be the case, caproic acid is adsorbed with its chain parallel or attached to the underlying carbon atoms. It appears that 1 mol. of caproic acid can displace only two carboxyl groups (compare formic, aminoacetic, and oxalic acids). In every case, complete poisoning would be obtained when $3{\cdot}1 \times 10^{-4}$ g.-mol. (mean value of *A*) of caproic acid is adsorbed per g. of charcoal.

The total carbon area active for oxidation is thus identical for all the four acids investigated on this particular charcoal, whilst the rates of oxidation of the various acids at their respective maxima

TABLE II.

Acid.	M.	$X \times 10^4$.	k.	P.	$d \times 10^4$.	$a \times 10^4$.	d/a.	$D \times 10^4$.	$A \times 10^4$.
Oxalic	0·015	4·5	0·75	62	2·1	2·0	1·05	3·4	3·2
„	„	„	„	91	3·2	3·1	1·03	3·5	3·4
Formic	0·5	6·2	0·55	11	0·6	0·4	1·5	5·4	3·6
„	„	„	„	69	4·1	2·05	2·0	6·0	2·9
Malonic	0·05	7·6	0·43	48	2·1	1·3	1·6	4·4	2·7
„	„	„	„	70	3·2	2·0	1·6	4·6	2·9
Aminoacetic	0·50	6·8	0·22	37	2·1	1·1	1·9	5·9	3·0
„	„	„	„	88	5·4	2·6	2·1	6·1	3·0
Oxalic *	0·015	4·5	0·75	95	1·33			1·4	
Formic * ...	0·5	6·2	0·55	93	3·0			3·25	

M = Concentration for maximum rate of oxidation (g.-mol. per litre).
X = Acid adsorbed on unpoisoned charcoal (g.-mol. per g. of charcoal).
k = Reaction velocity on „ „ (c.c. O_2 per g. of C per hr.).
P = % Poisoning.
d = Acid displaced for P % poisoning (g.-mols. per g. of C).
a = Caproic acid adsorbed for P % poisoning (g.-mols. per g. of C).
D = Acid displaced for complete poisoning (g.-mols. per g. of C).
A = Caproic adsorbed „ „ „ („ „ „).

(D and A are calculated on the assumption that the degree of poisoning is proportional to the amount of acid displaced, or of poison adsorbed, although the results show that this is not strictly accurate.)

* These were poisoned with saturated ethylene dibromide in 4% aqueous alcohol. Malonic and aminoacetic acids were not poisoned readily by this substance.

are by no means identical. We may attempt a revaluation of the active area per g. of charcoal from these data. The total specific area of the charcoal, as determined by the saturation point of methylene-blue (see Part I), is 185 sq. m. per g. Since there is some doubt as to whether the methylene-blue method actually gives the total area, owing to the inability of the large molecules of the dyestuff to penetrate into the micropores of the charcoal, the surface saturation point of oxalic acid was determined from the adsorption isotherm.

From Table I, it is noted that 37×10^{-4} g.-mol. is adsorbed per g. from a $0{\cdot}75M$-solution; the adsorption isotherm is inconveniently flat near the maximum, but we may assume the maximum to be at *ca.* 40×10^{-4} g.-mol. per g.

The area of the adsorbed oxalic acid molecule is unknown, but, regarding it as equal to that of two expanded carboxyl groups, we obtain 50 Å. per mol., giving an area of 1212 sq. m. per g., or some seven times greater than that given by the methylene-blue method. The amount of oxalic acid displaced on complete poisoning by caproic acid is $3{\cdot}5 \times 10^{-4}$ g.-mol. per g., or 8·75% of the total

surface is effective; on poisoning with ethylene dibromide, $1{\cdot}4 \times 10^{-4}$ g.-mol. per g. is displaced, or 3·5% of the total surface is effective, when the oxalic acid is employed as a means of evaluating the total area. These values are considerably smaller than those given previously where methylene-blue was employed. They are probably more accurate, in that the amount of poison adsorbed agrees closely with the amount of acid displaced, the poison being very much more preferential in its action than amyl alcohol.

Experiments with Promoted Charcoal.—An active promoted charcoal was prepared from sugar, carbamide, and ferric chloride, and the rates of oxidation of the four acids were determined on specimens of this charcoal. The oxidations due to the presence of the Fe–C–N and Fe–C areas were determined in the manner previously described by poisoning with solutions of potassium thiocyanate and potassium cyanide. The relative rates of oxidation of the four acids on the unpoisoned promoted charcoal are:

Acid.	C.c. of O_2 per g. per hr.	Relative rate.	Relative rate on sugar-charcoal.
Aminoacetic	1·2	1	1
Malonic	0·74	0·6	2
Formic	4·4	3·6	2·5
Oxalic	5·3	4·4	3·4

It will be noted that malonic acid is oxidised relatively slowly on the promoted charcoal. It was found also that there was no appreciable alteration in its rate of oxidation on the addition of either potassium cyanide or potassium thiocyanate, an indication that the promoted areas in the charcoal are not effective in oxidising this acid. The final product of oxidation of malonic acid (see Part I) is glyoxylic acid, and it is probable that hydroxymalonic acid is formed as an intermediate oxidation product. This hydroxy-acid may poison the iron in the presence of oxygen by the formation of a complex similar to that formed by ferrous salts with hydrogen peroxide in Fenton's test for hydroxy-acids. The transient purple of this test can indeed be obtained on application of Fenton's reagents to a solution of malonic acid which has been agitated with charcoal in the air for some hours. The two breaks in the velocity–poisoning curves indicative of the presence of two promoted areas (compare Pt. III) could be obtained with both aminoacetic and formic acids, and show that these acids, like oxalic acid, oxidise at different speeds on the three types of surface (the Fe–C–N, Fe–C, and C–C areas) present in the charcoal.

It was found difficult to obtain accurate values for the effective areas of these promoted areas for formic and aminoacetic acids, since the iron is slowly extracted from the charcoal in the presence

of these acids. The approximate values are given in the following table:

Acid.	Velocity (c.c. of O_2 per g. per hr.) on Fe–C–N area.	Fe–C area.
Aminoacetic	1·08	0·009
Formic	3·90	0·042
Oxalic	4·37	0·049

The relative areas were found to be 9·1 sq. m. per g. for the Fe–C area and 5·5 sq. m. per g. for the Fe–C–N area. It will be noted that the relative rates of oxidation for the acids on the promoted Fe–C–N area are not widely different from those on the sugar-charcoal, and although the experimental error is much greater on account of the small velocities observed, a similar sequence in velocities is noted on the Fe–C area. We may conclude that the active patches on such charcoals are definite in extent and possess the property of oxidising a number of different acids, and that the difference in speed of reaction for different acids is to be attributed to the ease of reaction of the acid with the excited oxygen. This is probably present on the surface of the charcoal in the form of a peroxide which may be desorbed from the surface by excess of acid.

That the ease of oxidation of these fatty acids in aqueous solution follows the same sequence as the reaction velocity of catalytic oxidation at charcoal surfaces was demonstrated by measuring the depolarising capacity of solutions of these acids. These were determined by electrolysis between a small platinum cathode and a large, smooth platinum anode of an $N/5$-solution of sulphuric acid which was also N with respect to the acid under investigation. With the aid of a normal calomel electrode, salt junction, and Wheatstone bridge, the anode potential could be determined for various current densities at 25°. The curves obtained for the various acids are depicted in the figure.

It will be seen that neither acetic nor succinic acid exerts any appreciable depolarising action on the anodic evolution of oxygen, and neither of these acids is oxidised at observable rates with the charcoals hitherto examined by us; on the other hand, the depolarising powers of oxalic, formic, and aminoacetic acids fall in the order of their rates of oxidation on charcoal surfaces. Tyrosine, a substance readily oxidised at charcoal surfaces, is included for comparison.

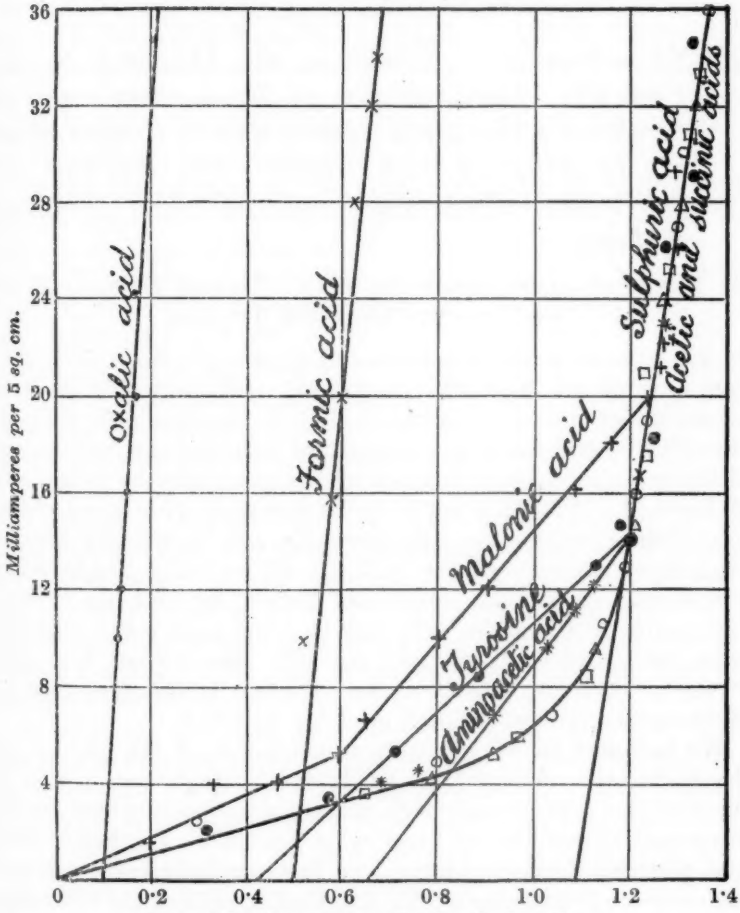
Summary.

The oxidation rates and the effects of poisoning with caproic acid on charcoal surfaces have been examined for formic, oxalic, malonic, and aminoacetic acids. It is found that the amounts

of poison absorbed required to inhibit the oxidation of these acids are identical. The effective catalytic area is found by this method to be about 4—8% of the total surface. With the exception of

FIG. 1.

Electrolytic oxidation of acids on a platinum anode (21 *sq. cm. area*).



$N/5$-H_2SO_4 ○. $N/5$-H_2SO_4 + N acetic acid □. $N/5$-H_2SO_4 + N-succinic acid △. $N/5$-H_2SO_4 + N-aminoacetic acid ✱. $N/5$-H_2SO_4 + $N/10$-tyrosine ●. $N/5$-H_2SO_4 + N-malonic acid +. $N/5$-H_2SO_4 + N-formic acid ×. $N/5$-H_2SO_4 + N-oxalic acid ●.

malonic acid, all these acids oxidise more rapidly on the promoted Fe–C–N and Fe–C areas than on pure charcoal. The poisoning of the promoted charcoal in the case of malonic acid is attributed to the hydroxy-acid formed as an intermediate oxidation product.

The velocities of oxidation at their respective maximum rates are shown to follow the order of depolarisation for oxygen liberated at a platinum electrode.

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CCCXI.—*Orientation Effects in the Diphenyl Series. Part IV. The Reduction of Bandrowski's and of Strakosch's Dinitrobenzidines, and the Condensation of the Products with Benzil. The Nitration of* 2-*Nitrodiacetylbenzidine and of* 4:4′-*Dibromodiphenyl.*

By RAYMOND JAMES WOOD LE FÈVRE, DANIEL DONALD MOIR, and EUSTACE EBENEZER TURNER.

IT was recently shown (Le Fèvre and Turner, J., 1926, 1759) that Cain's supposed 3:3′-dinitrobenzidine (Bandrowski's dinitrobenzidine) was the 2:3′-derivative, but, as was then fully realised, one difficulty still remained in connexion with the supposed identity of the two quinoxalines obtained by Cain and later by Brady and McHugh (J., 1923, **123**, 2047) by condensation with benzil of the tetra-amines derived from Bandrowski's and Strakosch's dinitrobenzidines. In view of the difficulty of purifying Bandrowski's compound (compare Le Fèvre and Turner, *loc. cit.*), an obvious explanation of the above facts was that the quinoxaline obtained from the Bandrowski material actually was derived from the Strakosch product, present as an impurity in the specimens of Bandrowski's dinitrobenzidine used for reduction.

We hesitated to advance this as a solution of the problem in the light of the conclusions of Brady and McHugh, but, in view of the fact that the Bandrowski's dinitrobenzidine prepared by Le Fèvre and Turner (*loc. cit.*) had m. p. 236—237°, *i.e.*, higher than that given by previous workers, we have carefully re-investigated the compounds concerned. We find that, in spite of the difficulties mentioned above, Bandrowski's dinitrobenzidine, *melting at* 233°, does, on reduction, followed by treatment with benzil in glacial acetic acid, give, as the most readily isolable product, a quinoxaline which is undoubtedly identical with that derived normally from 3:3′:4:4′-tetra-aminodiphenyl, and that therefore the initial Bandrowski's dinitrobenzidine must have contained some 3:3′-dinitrobenzidine.

There is a very marked difference in the behaviour of the two

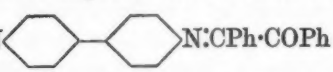
tetra-amines when treated with benzil. With that derived from Strakosch's dinitrobenzidine, a copious precipitate is obtained, but with that derived from Bandrowski's dinitrobenzidine (m. p. 233°, or a little lower), only a *small quantity* of precipitate results. The smallness of the yield was not mentioned by previous authors, and the foregoing explanation was therefore not suspected. The amount of Strakosch's dinitrobenzidine necessary to depress the m. p. of pure Bandrowski's dinitrobenzidine from 236—237° to 233° has been estimated, by examining artificial mixtures, as 2—3%. Such a proportion is in approximate agreement with the yields of quinoxaline obtained from various samples (see Experimental).

During the progress of this work, Hodgson (J., 1926, 2384) showed that some 3 : 3′-dinitrobenzidine was *formed* during the nitration of diphthalylbenzidine, but he did not attempt to demonstrate the presence of the 3 : 3′-isomeride in what has always been called Bandrowski's dinitrobenzidine, *i.e.*, a compound melting in the neighbourhood of 233°.

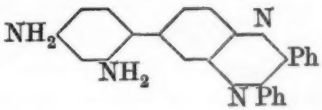
Methods previously described (Brunner and Witt, *Ber.*, 1887, **20**, 1024; Brady and McHugh, *loc. cit.*) for the reduction of Bandrowski's dinitrobenzidine proved unsatisfactory, but it was readily effected by iron powder, water, and ferric chloride.

Brady and McHugh showed that the two tetra-amines behaved very differently towards nitrous acid. A marked contrast was also observed when each was warmed in dilute acetic acid solution with acetic anhydride. In one case (2 : 3′ : 4 : 4′), bunches of white needles slowly separated from a purple solution, whilst in the other case there was immediate formation of an iridescent cream-coloured paste of minute needles. The compounds formed were the expected *tetra-acetyl* derivatives.

It was shown (Le Fèvre and Turner, J., 1926, 2476) that Cain's benzidine–benzil condensation product was dibenzoylbenzylidenebenzidine (I). 2 : 3′ : 4 : 4′-Tetra-aminodiphenyl (Bandrowski's tetra-amine) would therefore be expected to condense rapidly with

(I.) 

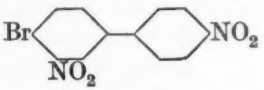
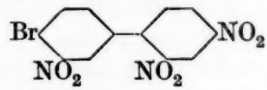
benzil in cold glacial acetic acid solution to give (II), which should condense further with benzil only at higher temperatures. We

(II.) 

find that (II) is soluble in cold acetic acid, and that on heating the solution in which it is formed it undergoes further condensation

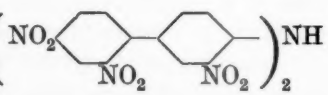
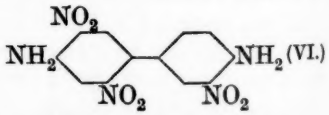
with production of what is evidently a mixture of the two benzoylbenzylidene derivatives and the dibenzoylbenzylidene derivative corresponding with (I).

Although we have improved upon the usual process for obtaining Bandrowski's dinitrobenzidine, we attempted to prepare the corresponding tetra-amine without recourse to the parent dinitrobenzidine. 4-Bromo-4′-nitrodiphenyl was nitrated to give 4-*bromo*-3 : 4′-*dinitrodiphenyl* (III) which on further nitration gave 4-bromo-2′ : 3 : 4′-trinitrodiphenyl (IV) (Le Fèvre and Turner, J., 1926, 2041). Small quantities of the latter compound were readily convertible into 2′ : 3 : 4′-*trinitro*-4-*aminodiphenyl*, but the large-scale conversion proved unsatisfactory. The reduction of the trinitroamine was accordingly not fully investigated.

(III.)   (IV.)

When (IV) was dissolved in boiling nitrobenzene, and dry ammonia was passed through, a bright yellow substance was obtained, apparently 4 : 4′-*bis*-op-*dinitrophenyl*-2 : 2′-*dinitrodiphenylamine* (V). The results of similarly treating other compounds containing reactive halogen atoms are recorded in the experimental part.

When attempting to prepare 2 : 3′-dinitrobenzidine from 2-nitrodiacetylbenzidine (Le Fèvre and Turner, *loc. cit.*), we observed that an impure product occasionally results, apparently owing to overnitration. We have now obtained from such products, by application of the method used for preparing Bandrowski's dinitrobenzidine from diphthalylbenzidine, the sparingly soluble *sulphate* of 2 : 5 : 3′-*trinitrobenzidine* (VI), the constitution of which is proved

(V.)   (VI.)

by its conversion by the perbromide method into 4 : 4′-*dibromo*-2 : 5 : 3′-*trinitrodiphenyl*, this in turn being identified by its ready conversion into a *di*piperidino-compound, *viz.*, 2 : 5 : 3′-*trinitro*-4 : 4′-*dipiperidinodiphenyl* (VII).

(VII.)

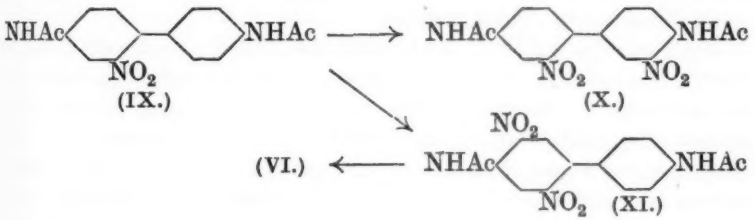
(VIII.)

Lellmann (*Ber.*, 1882, **15**, 2838) had previously isolated by overnitration of dibromodiphenyl a trinitro-derivative, having a m. p.

some 70° lower than that of the above compound. Lellmann's compound is, however, the isomeric 4 : 4′-*dibromo*-2 : 3′ : 5′-*trinitrodiphenyl* (XIV), since 4-*bromo*-2 : 3′ : 5′-*trinitro*-4′-*piperidinodiphenyl* (VIII) is formed from it with great readiness.

Comparison of the results now obtained with those previously recorded (this series) appears to show that, amongst the examples studied, the *op*- directive influence of groups decreases in the order NHAc > *p*-NHAc·C_6H_4 > *p*-Br·C_6H_4 > Br, the first being very powerful. In the light of this, it is possible to discuss the complete nitration of 2-nitrodiacetylbenzidine (IX) and of 4 : 4′-dibromo-2-nitrodiphenyl.

The former is now known to give as the main product 2 : 3′-dinitrodiacetylbenzidine (X), but since it has been shown (Bell and Kenyon, J., 1926, 2705) that 4-acetamidodiphenyl nitrates in position 3, *i.e.*, in the nucleus containing the acetamido-group, it would not be surprising, particularly in view of the now established powerful directive effect of this group, if some of the isomeric 2 : 5-compound (XI) were also formed. Further nitration of a



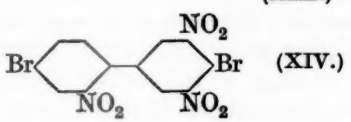
mixture of (X) and (XI) would only be expected to affect (XI). We have actually found that (X) is unaffected by fuming nitric acid at 25°, *i.e.*, under conditions more drastic than those under which the trinitro-compound (VI) was originally formed. The nitration of 2-nitrodiacetylbenzidine, therefore, in all probability proceeds in accordance with the scheme outlined above.

The nitration of 4 : 4′-dibromo-2-nitrodiphenyl has previously been shown (Dennett and Turner, J., 1926, 476) to be controlled entirely by the bromine atom in the ring B (XII), since nucleus A is rendered ineffective owing to the presence of the nitro-group : 4 : 4′-dibromo-2 : 3′-dinitrodiphenyl is therefore quantitatively produced. In the further nitration of this compound, each nucleus will be as ineffective upon the other as was A in (XII); that is, entry of the third nitro-group will be controlled only by the nitro-group and bromine atom present in the nucleus attacked. In nucleus B (XIII) these groups will both favour nitration in position 5, whilst in A (XIII) they have antagonistic influences. Nitration

therefore occurs in B, with formation of the above 4 : 4′-dibromo-2 : 3′ : 5′-trinitrodiphenyl (XIV).

(XII.)

(XIII.)



(XIV.)

EXPERIMENTAL.

Preparation of 2 : 3′-Dinitrobenzidine.—The following modification of the usual process is more satisfactory, particularly as regards yield: Powdered diphthalylbenzidine (270 g.) was slowly dissolved in 1800 c.c. of fuming nitric acid (*d* 1·5), the temperature not being allowed to rise above 10°. After 15 minutes, the mixture was poured on 5 kg. of crushed ice, the resulting light yellow precipitate being washed first with boiling water and then with hot methylated spirit (yield, 350 g.).

For hydrolysis, 270 g. of the above product, previously dried at 100°, were dissolved in 1200 c.c. of concentrated sulphuric acid, and the solution was heated at 135—140° for 20 minutes. After being cooled, the acid solution was poured into 5 l. of water, the temperature not being controlled. The precipitate first formed redissolved as the temperature rose, and the nearly clear solution, after filtration, deposited long, yellow-brown needles when cooled. These were collected and crystallised from dilute sulphuric acid (1 : 4 by vol.). The crystals so obtained were ground with aqueous ammonia, and the red base (m. p. 225°) was filtered off. One crystallisation from phenol–alcohol gave a definitely crystalline specimen, m. p. 233°. Two further crystallisations raised the m. p. to 234—235°, and to 236—237° (uncorr.), respectively, the final product being pure 2 : 3′-dinitrobenzidine.

Melting Points of Mixtures of 2 : 3′- and 3 : 3′-Dinitrobenzidines.—The specimens of the two bases used had m. p. 243—244° and 281—282° (corr.) respectively. A mixture containing 90% of 2 : 3′-base and 10% of 3 : 3′-base shrank at about 224°, showed definite signs of melting at 233°, and ran to a liquid at 237°; one containing 94·8% of 2 : 3′- and 5·2% of 3 : 3′ base reached the same three stages respectively at 226°, 236°, and 238·6°; and the 97·6–2·4% mixture at 238°, 239·9°, and 241·4°. The above figures were obtained by the use of a completely immersed, short-stem standard thermometer. The corresponding uncorrected figures,

taken simultaneously with an ordinary thermometer, were: 218°, 227°, 231°; 220—221°, 229°, 232°; and 232°, 233°, 235°, respectively.

Reduction of Bandrowski's Dinitrobenzidine.—Preliminary experiments showed (1) that the tetra-amine is readily soluble in water, and (2) that the solution rapidly oxidises in the air. The following procedure was therefore adopted: 100 G. of iron powder were thoroughly wetted with 100 c.c. of water at 100°; 10 g. of 2 : 3′-dinitrobenzidine were then added, and the whole was well mixed. On the addition of a little ferric chloride, reduction proceeded vigorously, and was completed by ½ hour's heating with continuous stirring. Water was added, and the tetra-amine obtained in clear aqueous solution by filtration. Evaporation of this in a current of carbon dioxide (*a*) gave 2 : 3′ : 4 : 4′-tetra-aminodiphenyl as a purplish solid.

Reduction of Strakosch's Dinitrobenzidine.—10 G. of the dinitrobenzidine were shaken in a litre flask with 150 c.c. of methylated spirit until in fine suspension. 200 C.c. of water were added, followed by 70 g. of sodium hyposulphite, and the mixture was heated on the boiling water-bath for an hour. During this time, the colour changed from red to pale grey, and the suspended solid almost completely dissolved. The alcohol was then distilled off, the residue extracted with a mixture of water (150 c.c.) and concentrated hydrochloric acid (150 c.c.), the extract filtered, and the filtrate evaporated to about 2/3 of its original bulk. On cooling, pale brown needles of 3 : 3′ : 4 : 4′-tetra-aminodiphenyl hydrochloride separated. These, after being crystallised from dilute hydrochloric acid, were ground with aqueous ammonia; the liberated base crystallised from a mixture of phenol and alcohol in greyish plates, m. p. about 172—173° (Found: N, 26·5, 26·3. Calc.: N, 26·2%).

Condensation of 2 : 3′ : 4 : 4′-Tetra-aminodiphenyl with Benzil.—(a) *In the cold.* The flask in which the evaporation and extraction (*a* above) had been effected was tared, after its contents had been dried, and the soluble material was extracted four times with 10 c.c. of warm glacial acetic acid. Filtration from a considerable quantity of dark-coloured insoluble material enabled the amount of tetra-amine in solution to be calculated (generally of the order of 2 g.). A solution of the required quantity of benzil in cold glacial acetic acid was added to the cooled filtrate. After some minutes, crystallisation could be induced by scratching, but even after 12 hours the amount of greenish-yellow precipitate was quite small. Reduction of 10 g. lots of specimens of Bandrowski's dinitrobenzidine, melting at 225—226°, 233°, and 237° (uncorr.), gave 1·9, 1·1, and 0·0 g. of "quinoxaline" respectively. The crystals appeared as radiating bunches of needles when examined under

the microscope, and melted in the crude state at 292—300°. The product crystallised readily from salicylaldehyde (originally used as a reagent to detect a free amino-group) in long, thin, straw-coloured plates, m. p. 308—309° (uncorr.). Admixture with an authentic specimen of Strakosch's quinoxaline did not depress this m.p. (Cain, Coulthard, and Micklethwait, *loc. cit.*; Brady and McHugh, *loc. cit.*) (Found : N, 10·7. Calc. : 10·0%). The mother-liquors from this crystallisation were dark coloured, indicating that the salicylaldehyde had reacted with the green impurities in the crude quinoxaline (see below).

(b) *At* 100°. In earlier experiments, condensation was attempted using excess of benzil in glacial acetic acid at 100°. In most cases, no precipitation occurred, even on scratching. Dilution with water produced a gummy deposit, from which dilute alcohol extracted a yellowish-green powder, soluble in glacial acetic acid, xylene, benzene, chloroform, and acetone, but obviously a mixture, with a m. p. range of about 30°.

A very marked reaction occurred when the product was heated with salicylaldehyde, water being eliminated.

Condensation of 3 : 3′ : 4 : 4′*-Tetra-aminodiphenyl with Benzil.*—To 1 g. of tetra-amine dissolved in 15 c.c. of glacial acetic acid was added a solution of 2 g. of benzil in 5 c.c. of the same solvent. A precipitate was formed suddenly, and this, when viewed under the microscope, appeared as stout needles. Alcohol was added, the solid filtered, re-heated with alcohol, and then dried at 100°. The cream-coloured powder (m. p. crude, 303—306°) separated from salicylaldehyde in straw-coloured plates, m. p. 308° (Found : N, 10·7%). It was very sparingly soluble in glacial acetic acid and acetone, more soluble in benzene, readily soluble in chloroform, and crystallised well from xylene in parallelograms, m. p. 308° (uncorr.), 313° (corr.).

Colour Reactions with Concentrated Sulphuric Acid.—The benzil condensation products derived both from Bandrowski's and from Strakosch's tetra-amines gave nearly identical purplish-red colorations with concentrated sulphuric acid. The colour is clearly due to the quinoxaline structure, and not to the possible presence of benzoylbenzylidene groupings, since αβ-diphenylquinoxaline gave a reddish-orange colour, whilst dibenzoylbenzylidenebenzidine merely dissolved to a normal yellow solution, which after a few minutes set to a white mass of benzidine sulphate. The other colours disappear on the addition of water or on exposure to the air (compare Brunner and Witt, *loc. cit.*).

Preparation of 4*-Bromo-*2′ : 3 : 4′*-trinitrodiphenyl.*—The following method proved more satisfactory than that used in Part III of this

series, as it avoided numerous wasteful crystallisations : An intimate mixture of 100 g. of 4-bromo-4′-nitrodiphenyl and 52 g. of potassium nitrate was slowly added to 300 c.c. of concentrated sulphuric acid at 70—80°. The resulting solution was heated at 90° for ¼ hour, then cooled and poured into water. Crystallisation of the resulting precipitate from glacial acetic acid gave 4-*bromo*-3 : 4′-*dinitrodiphenyl* as dull white needles, m. p. 135° (Found : Br, 24·8. $C_{12}H_7O_4N_2Br$ requires Br, 24·8%). A mixture of 8 g. of the latter with 4 g. of potassium nitrate was nitrated in 60 c.c. of concentrated sulphuric acid under the above conditions. The product melted at 176° after one crystallisation from glacial acetic acid.

2′ : 3 : 4′-*Trinitro*-4-*aminodiphenyl*.—4-Bromo-2′ : 3 : 4′-trinitrodiphenyl (3 g.) was heated with saturated alcoholic ammonia (15 c.c.) in a sealed tube at 150° for 8—10 hours. The product was filtered off, dried, and crystallised from glacial acetic acid. It formed yellowish-orange needles, m. p. 192—193° (Found : N, 18·7. $C_{12}H_8O_6N_4$ requires N, 18·4%). This procedure proving very tedious, the following modification was attempted : 20 G. of 4-bromo-2′ : 3 : 4′-trinitrodiphenyl were dissolved in 200 c.c. of boiling nitrobenzene, and a current of dry ammonia was passed through the solution for 2 hours. A yellow solid soon began to separate, and, after cooling, it was collected, washed with benzene, dried, and crystallised from phenol–alcohol, forming bright yellow needles, m. p. 256—257° (Found : N, 17·0. $C_{24}H_{13}O_{12}N_5$ requires N, 16·6%). The analysis and the fact that the substance separates unchanged after being heated with salicylaldehyde prove it to be 4 : 4′-*bis*-o*p*-*dinitrophenyl*-2 : 2′-*dinitrodiphenylamine* (V). Its low solubility in solvents prevented a determination of its molecular weight.

Action of Ammonia upon Boiling Nitrobenzene Solutions of other Halogeno-nitro-compounds.—(*a*) Picryl chloride (10 g.) was dissolved in boiling nitrobenzene (50 c.c.), and ammonia passed in for 2 hours, although solid had begun to separate very soon. The mixture was cooled and the resulting solid was crystallised from glacial acetic acid and identified as trinitroaniline, m. p. 187—188°.

(*b*) 1-Chloro-2 : 4-dinitrobenzene (20 g.), treated similarly (50 c.c. of nitrobenzene), also gave a precipitate, which separated from glacial acetic acid, and had m. p. 180—182°. It was thus 2 : 4-dinitroaniline.

(*c*) 2 : 5-Dichloronitrobenzene (10 g.) dissolved in 25 c.c. of boiling nitrobenzene was apparently unaffected by ammonia.

(*d*) 4 : 4′-Dibromo-2 : 3′-dinitrodiphenyl was partially converted into the corresponding bromo-amino-compound under the above conditions.

Isolation of 2 : 5 : 3′-*Trinitrobenzidine.*—The crude hydrolysis product resulting from a nitration of 70 g. of 2-nitrodiacetylbenzidine was boiled with dilute sulphuric acid, the extract filtered, allowed to crystallise, and the resulting *sulphate* again crystallised from dilute sulphuric acid. It was ground with aqueous ammonia, and the liberated base crystallised three times from phenol–alcohol, dark red needles, m. p. 276°, being obtained (Found : N, 21·6. $C_{12}H_9O_6N_5$ requires N, 21·9%).

The *diacetyl* derivative was a yellow substance, m. p. above 300°.

4 : 4′-*Dibromo*-2 : 5 : 3′-*trinitrodiphenyl.*—A solution of trinitrobenzidine (3·2 g.) in 20 c.c. of concentrated sulphuric acid was diazotised in the usual manner by 1·4 g. of solid sodium nitrite. The solution was diluted by the addition of 100 g. of ice, and filtered; 3 c.c. of bromine dissolved in 12 c.c. of hydrobromic acid were added, and the oily *perbromide* which separated solidified after 15 minutes, and was filtered off. Decomposition by heating with 40 c.c. of glacial acetic acid proceeded smoothly, and gave rise to a cream-coloured, crystalline precipitate of 4 : 4′-*dibromo*-2 : 5 : 3′-*trinitrodiphenyl*, which separated from about 250 c.c. of glacial acetic acid in wads of needles, m. p. 251—252°. The substance reacted readily with piperidine to give the 4 : 4′-*dipiperidino*-compound, which crystallised from rectified spirit in matted needles, m. p. 160° (Found : N, 15·8. $C_{22}H_{25}O_6N_5$ requires N, 15·4%).

Nitration of 4 : 4′-*Dibromo*-2 : 3′-*dinitrodiphenyl.*—When a solution of this compound in nitric acid (*d* 1·5) was allowed to stand, according to Lellmann's instructions, it remained unaffected. 3 G. of the dinitro-compound in 30 c.c. of a mixture (1 : 5 by vol.) of concentrated sulphuric acid and nitric acid (*d* 1·5) were left for 20 hours. Water was then added, and the precipitate extracted with a large bulk of alcohol. The residue crystallised from toluene in colourless needles, m. p. 176—177°, and reacted very vigorously with piperidine, even in the cold, to give the orange-coloured 4-*bromo*-2 : 3′ : 5′-*trinitro*-4′-*piperidinodiphenyl*, which, after being crystallised from much glacial acetic acid, melted at 194° (Found : N, 12·5. $C_{17}H_{15}O_6N_4Br$ requires N, 12·4%).

3 : 4′-*Dinitro*-4-*anilinodiphenyl.*—This substance was obtained by heating 4-bromo-3 : 4′-dinitrodiphenyl with excess of aniline at the b. p. of the latter for 5 minutes. It separated from glacial acetic acid in orange leaflets, m. p. 155—156°.

3 : 2′ : 4′-*Trinitro*-4-*anilino- and* -4-*methylanilino-diphenyl.*—These were readily obtained by heating 4-bromo-3 : 2′ : 4′-trinitrodiphenyl with excess of aniline and methylaniline respectively. The *anilino*-derivative crystallises from glacial acetic acid in orange-red leaflets,

m. p. 190—191°, and the *methylanilino*-derivative from the same solvent in deep red leaflets, m. p. 212°.

Part of the expenses of this investigation were met by grants allocated to two of us by the Chemical Society, and one of us (R. J. W. Le F.) is indebted to the Advisory Committee of the Department of Scientific and Industrial Research for a maintenance grant.

EAST LONDON COLLEGE,
UNIVERSITY OF LONDON. [*Received, July 25th*, 1927.]

CCCXII.—*The Preparation of 2 : 5-Dihydroxybenzaldehyde (Gentisaldehyde).*

By HERBERT HENRY HODGSON and HERBERT GREENSMITH BEARD.

NEUBAUER and FLATOW (*Z. physiol. Chem.*, 1907, **52**, 375) prepared 2 : 5-dihydroxybenzaldehyde by the oxidation of salicylaldehyde, but the present method with *m*-hydroxybenzaldehyde as initial material gives an improved yield of a less crude product.

A solution of *m*-hydroxybenzaldehyde (61 g.) and sodium hydroxide (25 g.) in water (400 c.c.), while being vigorously stirred and kept at 30—35°, is treated simultaneously from separate dropping-funnels with aqueous solutions of potassium persulphate (150 g. in 1500 c.c.) and sodium hydroxide (200 c.c.; 40%), the additions being made during 90 minutes at such rates that the mixture is always alkaline. After 36 hours' standing, the deep brown solution is rendered faintly acidic (Congo paper) with concentrated hydrochloric acid, and unchanged *m*-hydroxybenzaldehyde (31 g.) is extracted by ether. The solution is then strongly acidified (350 c.c. of concentrated hydrochloric acid) and heated slowly to 70°, the dark brown, amorphous precipitate (5 g.), which forms gradually, being filtered off. (This substance, which chars above 330°, is almost insoluble in all organic solvents except boiling glacial acetic acid, but readily soluble in aqueous sodium carbonate; it contains the aldehyde group, as shown by formation of a p-*nitrophenylhydrazone* which gives the characteristic magenta colour with alkalis, and invariably constitutes about 40% of the yield.) The 2 : 5-dihydroxybenzaldehyde is extracted from the filtrate by ether, the ether is removed by evaporation, and the residue extracted by benzene; yield 13 g. (m. p. 89—92°). The substance crystallises from benzene in bright yellow needles, containing solvent of crystallisation, which rapidly effloresce at the ordinary temperature, leaving yellow needles, m. p. 98—99° (Tiemann and Müller, *Ber.*,

1881, **14**, 1986, give m. p. 99°). The aqueous solution gives a green colour with ferric chloride and red with sodium hydroxide. Identity was established with 2 : 5-dihydroxybenzaldehyde prepared by Neubauer and Flatow's method (*loc. cit.*), in which the corresponding yield of crude product was 12 g. (m. p. 83—90°). Substitution of ammonium for potassium persulphate, reduction in time of keeping, and oxidation at higher temperatures all produced lower yields.

2 : 5-Dihydroxybenzaldehyde could not be obtained from 2-nitro-5-hydroxybenzaldehyde by reduction, diazotisation, and any variation of decomposition procedure, although Sandmeyer treatment of the diazo-solution afforded 30% yields of 2-chloro- or 2-bromo-5-hydroxybenzaldehyde.

Derivatives. The p-*nitrophenylhydrazone* crystallises from glacial acetic acid in brick-red needles, m. p. 256—257° (decomp.) (Found: N, 15·6. $C_{13}H_{11}O_4N_3$ requires N, 15·4%). The *dibenzoate* separates from alcohol in slender, colourless needles, m. p. 106—107° (Found: C, 72·5; H, 4·1. $C_{21}H_{14}O_5$ requires C, 72·8; H, 4·0%), and is readily hydrolysed by cold 20% aqueous sodium hydroxide. The p-*nitrophenylhydrazone* of the dibenzoate crystallises from glacial acetic acid in fine, orange needles, m. p. 272° (Found: N, 9·0. $C_{27}H_{19}O_6N_3$ requires N, 8·7%).

Methylation in 10% aqueous sodium hydroxide solution with methyl sulphate (2 mols.) gives the dimethyl ether, which crystallises from dilute alcohol in colourless needles, m. p. 51° (Tiemann and Müller, *loc. cit.*, give m. p. 51°), and forms a p-*nitrophenylhydrazone*, red needles, m. p. 216° (Found: N, 14·7. $C_{14}H_{14}O_4N_3$ requires N, 14·6%), from glacial acetic acid. In this methylation a monomethyl ether may be isolated, after extraction of the dimethyl ether, by acidification and steam-distillation; it passes over and remains as a colourless oil with a vanillin-like odour, and gives a blue-black colour with ferric chloride and a bright yellow solution with aqueous sodium hydroxide, both tests being characteristic of 5-methoxysalicylaldehyde (Tiemann and Müller, *loc. cit.*); the p-*nitrophenylhydrazone* crystallises from glacial acetic acid in bright orange needles, m. p. 206° (Found: N, 15·4. $C_{13}H_{12}O_4N_3$ requires N, 15·3%).

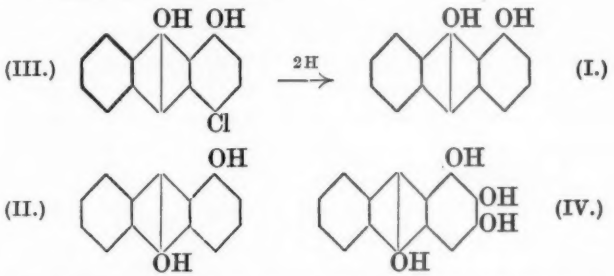
The authors thank the Department of Scientific and Industrial Research for a grant to one of them (H. G. B.), and the British Dyestuffs Corporation for gifts of chemicals.

TECHNICAL COLLEGE, HUDDERSFIELD. [*Received, August 6th*, 1927.]

CCCXIII.—*The Determination of the Structure of α-Hydroxyanthranols.*

By Albert Green.

The reduction of an α-hydroxyanthraquinone to the corresponding anthranol may occur in two ways: *e.g.*, 1-hydroxyanthraquinone may give 1 : 9-dihydroxyanthracene (I), 1 : 10-dihydroxyanthracene (II), or a mixture of these two.



By the reduction of alizarin 2-methyl ether, Miller and Perkin (J., 1925, **127**, 2684) obtained a mixture of the two possible isomeric anthranols, and were able to assign structures to them by observing the differences in the resistance of the derived benzanthrones to methylation. The use of the benzanthrone condensation in the determination of the structures of reactive substances such as the anthranols has disadvantages: purification of the products is tedious, and the yields are very small. Miller and Perkin (*loc. cit.*) themselves suggest that the poor yields are a result of the anthranols suffering alteration during heating with sulphuric acid for 1 hour at 125—130°. However, in a later paper (Cross and Perkin, this vol., p. 1297) improved methods of effecting the benzanthrone condensation are described.

The present method for deciding whether an anthranol is of type (I) or of type (II) depends on its reaction with thionyl chloride, which takes place at the ordinary temperature. It has been shown (J., 1924, **125**, 1450; 1926, 2198; this vol., pp. 500, 554) that two *ortho*-hydroxyl groups of a phenol always react with thionyl chloride to give a thionyl derivative, but that a similar compound is not given by *meta*- or *para*-dihydric phenols (J., 1926, 1428; this vol., p. 500). In view of the well-established resemblance between reactions shown by certain substituents in the *peri*-position (I) and those of the same groups in the *ortho*-position, it was anticipated that a compound of type (I) would yield a thionyl derivative, whereas one of type (II) would not.

These anticipations were verified by examining, in the first place,

the action of thionyl chloride on two substances of known structure, 1 : 8- and 1 : 5-dihydroxynaphthalene. When the former, in carbon disulphide–pyridine solution, is treated with the theoretical quantity of thionyl chloride it gives 1 : 8-*thionyldihydroxynaphthalene* in quantitative yield. The isomeric 1 : 5-dihydroxy-compound, on the contrary, does not give a thionyl derivative: all the methods of preparation previously described (*loc. cit.*) were used, and in every case the products were complex mixtures which always contained chlorine.

The method was then applied to three anthranols. Two of these, 1-hydroxyanthranol and 4-*chloro*-1-*hydroxyanthranol*, yield thionyl derivatives, and are therefore 1 : 9-dihydroxyanthracene (I) and 4-*chloro*-1 : 9-*dihydroxyanthracene* (III) respectively. In preparing the latter by reduction of 4-chloro-1-hydroxyanthraquinone, it was necessary to avoid over-reduction, which readily led to the replacement of the chlorine atom by hydrogen, with production of 1 : 9-dihydroxyanthracene (I).

The products of four experiments with anthragallol anthranol and thionyl chloride were all complex chlorine-containing mixtures, thus indicating that this anthranol is not 1 : 2 : 3 : 9-tetrahydroxyanthracene—for this would be expected to give a chlorine-free dithionyl derivative, since anthragallol itself yields 2 : 3-thionylanthragallol (J., 1926, 2202)—but is 1 : 2 : 3 : 10-tetrahydroxyanthracene (IV). This conclusion, which is based on negative evidence only, is contrary to that reached by Cross and Perkin (*loc. cit.*).

The anthranols used in this investigation were prepared from the corresponding anthraquinones by the method of Liebermann and Mamlock (*Ber.*, 1905, **38**, 1795), with tin and hydrochloric acid in acetic acid solution as reducing agent. This method was preferred to the more economical one of Breare and Perkin (J., 1923, **123**, 2606), who used a hydrochloric acid solution of stannous chloride, because the products were more easily purified.

The compounds described herein differ from the thionyl derivatives examined previously (*loc. cit.*) in that the thionyl group forms part of a six-atom ring, and is less reactive than one forming part of a heterocyclic structure of five atoms.

Experimental.

Preparation of Materials.—1 : 8-*Dihydroxynaphthalene.* A commercial specimen labelled "pure" contained more than 70% of impurities. The naphthol was eventually obtained pure by two methods: (I) A hot solution of the mixture in acetic anhydride and pyridine, on cooling, deposited practically pure 1 : 8-diacetoxy-

naphthalene. After one recrystallisation from acetic anhydride, this formed small, white plates of constant m. p. 155° (Erdmann, *Annalen*, 1888, **247**, 359, gives 147—148°) (Found: $CH_3{\cdot}CO$, 35·7. Calc.: 35·3%). The acetyl derivative was hydrolysed by the rapid addition of hydrochloric acid to its solution in hot acetic acid. After removal of some tarry matter by filtration through asbestos, a warm saturated solution of sulphur dioxide was added, and 1 : 8-dihydroxynaphthalene separated as hair-like, white needles, m. p. 144° (Found: C, 74·8; H, 5·1. Calc.: C, 75·0; H, 5·0%). (II) The impurities were very sparingly soluble in cold acetic acid, and were removed by fractional crystallisation. The acetic acid solutions, when diluted with water, yielded the naphthol as small, greyish-white crystals, which, after drying over sulphuric acid, melted at 142—143° (Found: C, 74·8; H, 5·2%). 1 : 8-Dihydroxynaphthalene dissolves in concentrated sulphuric acid with a greenish-gold colour, and its colourless solution in alcohol becomes dark green on the addition of ferric chloride.

The anthraquinones, which were converted into the anthranols, were obtained by the hydrolysis of the purified acetyl derivatives (compare J., 1926, 1431, 2199).

1 : 9-*Dihydroxyanthracene* (1-*Hydroxyanthranol*). This was obtained, by treating the hot acetic acid solution of the diacetate with hydrochloric acid, as faintly yellow, square plates, m. p. 142° (Found: C, 79·9; H, 4·9. Calc.: C, 80·0; H, 4·8%). The diacetate separated from a mixture of acetic anhydride and pyridine in short, pale yellow, six-sided prisms, m. p. 211° (Found: $CH_3{\cdot}CO$, 29·3. Calc.: $CH_3{\cdot}CO$, 29·3%).

4-*Chloro*-1 : 9-*dihydroxyanthracene* (4-*Chloro*-1-*hydroxyanthranol*). Owing to the ease with which 4-chloro-1-hydroxyanthraquinone was reduced to 1 : 9-dihydroxyanthracene, it was necessary to control the reduction carefully. The addition of hydrochloric acid to the acetic acid solution was stopped as soon as a test portion, added to excess of caustic soda, no longer showed a trace of the red colour of the sodium salt of the hydroxyanthraquinone (about 3 minutes). The solution was then rapidly decanted from the residual tin and cooled. The acetylated product, after recrystallisation from absolute alcohol, yielded 4-*chloro*-1 : 9-*diacetoxyanthracene* as rosettes of faintly yellow, fine needles, m. p. 157° [Found: Cl, 10·7; $CH_3{\cdot}CO$, 28·5. $C_{14}H_7O_2Cl(CH_3{\cdot}CO)_2$ requires Cl, 10·8; $CH_3{\cdot}CO$, 28·2%]. The hot acetic acid solution of these, when treated with hydrochloric acid, deposited 4-*chloro*-1 : 9-*dihydroxyanthracene* as pale greenish-yellow needles of constant m. p. 170—171° (Found: Cl, 14·5; *M*, cryoscopic in naphthalene, 245, 250. $C_{14}H_9O_2Cl$ requires Cl, 14·5%; *M*, 244·5), giving a bright greenish-gold solution

in concentrated sulphuric acid. Its solution in aqueous caustic soda is bright yellow, but on standing in air this is rapidly oxidised to the wine-red solution characteristic of the sodium salt of 4-chloro-1-hydroxyanthraquinone. In alcohol, the anthranol gives a pale greenish-yellow solution which becomes golden-brown on the addition of ferric chloride.

When 3·2 g. of 4-chloro-1 : 9-dihydroxyanthracene were reduced further by the method of Liebermann and Mamlock (*loc. cit.*) during 40 minutes, the product contained less than 1% of chlorine. Its solution in a mixture of warm pyridine and acetic anhydride deposited 2·1 g. of 1 : 9-diacetoxyanthracene, m. p. 208—209°, which after one recrystallisation from the same mixture melted at 210—211°, either alone or mixed with an authentic specimen (Found: $CH_3{\cdot}CO$, 29·6. Calc.: 29·3%).

The thionyl derivatives were prepared by the method adopted for 1 : 2-thionyldihydroxyanthracene (this vol., p. 557).

1 : 8-*Thionyldihydroxynaphthalene* (5·5 g. from 5·3 g. of the naphthol) separated from carbon disulphide in small, pearl-grey crystals, m. p. 97° (Found: C, 58·6; H, 2·9; S, 15·5; *M*, cryoscopic in naphthalene, 218, 210. $C_{10}H_6O_3S$ requires C, 58·3; H, 2·9; S, 15·5%; *M*, 206). It is stable to moisture and a specimen which had stood in air for 9 weeks showed no change in m. p. or in sulphur content. Cold aqueous caustic potash has no appreciable effect on the thionyl compound, but a hot alcoholic solution decomposes it with the production of a pale amethyst colour and the deposition of potassium sulphite. The thionyl compound dissolves in concentrated sulphuric acid with a dull amethyst colour, which changes to the greenish-gold of the naphthol when the solution is heated.

1 : 9-*Thionyldihydroxyanthracene* was obtained (5·0 g. from 4·8 g. of anthranol) from carbon disulphide as pale greenish-yellow plates, m. p. 115° (decomp.) (Found: C, 65·7; H, 3·2; S, 12·7; *M*, cryoscopic in naphthalene, 260, 264. $C_{14}H_8O_3S$ requires C, 65·6; H, 3·1; S, 12·5%; *M*, 256). It gives a greenish-gold solution in cold concentrated sulphuric acid; it is not appreciably soluble in cold caustic soda, but yields a light golden-brown solution on warming. The addition of ferric chloride to its pale yellow solution in alcohol produces no change.

4-*Chloro*-1 : 9-*thionyldihydroxyanthracene* crystallised from carbon disulphide in pale greenish-yellow plates, m. p. 123—124° (decomp.), 4·0 g. of anthranol yielding the same amount of thionyl derivative (Found: S, 11·2; Cl, 12·0; *M*, cryoscopic in naphthalene, 295. $C_{14}H_7O_3ClS$ requires S, 11·0; Cl, 12·2%; *M*, 290·5). The colour reactions are similar to those of 1 : 9-thionyldihydroxyanthracene.

The products obtained by treating 1 : 5-dihydroxynaphthalene with thionyl chloride showed chlorine contents varying from 14 to 22%; those from anthragallol anthranol contained sulphur in amounts varying from 0·7 to 15·6%, and chlorine from 2·1 to 21·5%. In all cases, the reactions and properties of the products pointed to their being complex substances formed by the condensation of several molecules.

The author desires to thank the Research Fund Committee of the Chemical Society for a grant which has defrayed a portion of the cost of this research, and also The British Alizarine Company, Limited, and The Scottish Dyes, Limited, for gifts of materials.

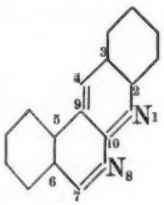
THE EDWARD DAVIES LABORATORIES,
UNIVERSITY COLLEGE OF WALES,
ABERYSTWYTH. [*Received, August 5th*, 1927.]

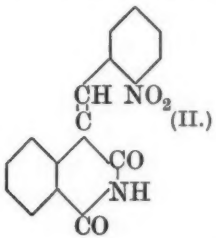
CCCXIV.—*Some Derivatives of* 2 : 3 : 5 : 6-*Dibenzo*-1 : 8-*naphthyridine.*

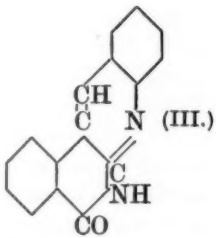
By ROBERT DOWNS HAWORTH and HERBERT SHEPHERD PINK.

DERIVATIVES of 2 : 3 : 5 : 6-dibenzo-1 : 8-naphthyridine (I) have not been previously described, and a method for their preparation from homophthalimide is now communicated. Dieckmann (*Ber.*, 1914, **47**, 1428) showed that the diethyl ester of homophthalic acid condensed with aldehydes, and homophthalimide is now shown to condense in a similar manner with *o*-nitrobenzaldehyde, giving excellent yields of o-*nitrobenzylidenehomophthalimide* (II) in pyridine solution in the presence of a trace of piperidine.

(I.)

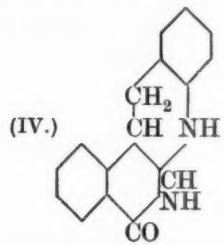


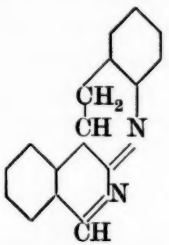




This sparingly soluble substance was reduced with stannous chloride in alcoholic solution to 7-*keto*-2 : 3 : 5 : 6-*dibenzo*-7 : 8-*dihydro*-1 : 8-*naphthyridine* (III), which is a pale yellow, very weak base, dissolving in concentrated mineral acids and being precipitated on dilution with water; it possesses marked acidic properties, however, owing to the presence of the *iso*carbostyril

grouping, and on treatment with dilute potassium or sodium hydroxide, bright yellow, sparingly soluble salts were obtained, the *sodium* salt being somewhat more soluble than the *potassium* salt. Owing to the sparing solubility of this ketodibenzodihydronaphthyridine, further reduction was difficult, but zinc dust in glacial acetic acid, saturated with hydrogen chloride, effected reduction to 7-*keto*-2 : 3 : 5 : 6-*dibenzo*-1 : 4 : 7 : 8 : 9 : 10-*hexahydro*-1 : 8-*naphthyridine* (IV), which is devoid of acidic properties, but readily yields a *monohydrochloride* and an amorphous *nitrosoamine*.





A similar series of compounds was obtained from the *N*-alkylated homophthalimides, the 8-β-*phenylethyl* and 8-β-*piperonylethyl* derivatives [as (II), (III), and (IV)] being described.

In attempting to reduce the carbonyl group of the ketodibenzodihydronaphthyridine (III), a small yield of a yellow *base*, $C_{16}H_{12}N_2$, was obtained by electrolytic reduction in alcoholic sulphuric acid solution. The same base was, however, more conveniently prepared (in 20% yield) by heating the keto-compound (III) with phosphorus oxychloride and pentachloride at 180° and reducing the unstable chloro-compound with phosphorus and hydriodic acid at 160—170°, the compound (IV) also being formed. The yellow base, $C_{16}H_{12}N_2$, was sparingly soluble in organic solvents and its dilute solutions exhibited an intense violet fluorescence. The two nitrogen atoms are both tertiary in character, since no nitrosoamine or acetyl derivative can be obtained. It is probably 2 : 3 : 5 : 6-*dibenzo*-4 : 9-*dihydro*-1 : 8-*naphthyridine* (V), for it dissolved in hot dilute hydrochloric acid to give a sparingly soluble *monohydrochloride*, and this monoacidic character is in agreement with the amidine structure suggested.

EXPERIMENTAL.

o-*Nitrobenzylidenehomophthalimide* (II).—Homophthalimide (20 g.), *o*-nitrobenzaldehyde (20 g.), pyridine (100 c.c.), and piperidine (0·5 c.c.) were boiled until homogeneous, and the heating was continued on the water-bath for 2 hours; the solution became

dark red and the product gradually separated on cooling in pale yellow needles, which recrystallised from pyridine in pale sulphur-yellow needles (35 g.), m. p. 236° (Found : N, 9·6. $C_{16}H_{10}O_4N_2$ requires N, 9·5%). o-*Nitrobenzylidenehomophthalimide* is sparingly soluble in the usual organic solvents, and gives a yellow solution in dilute aqueous sodium hydroxide.

o-*Nitrobenzylidene*-N-β-*phenylethylhomophthalimide* was prepared similarly from *o*-nitrobenzaldehyde and *N*-β-phenylethylhomophthalimide; it crystallised from pyridine in yellow needles, m. p. 146° (Found : N, 7·2. $C_{24}H_{18}O_4N_2$ requires N, 7·0%). o-*Nitrobenzylidene*-N-β-*piperonylethylhomophthalimide*, prepared from *o*-nitrobenzaldehyde and *N*-β-piperonylethylhomophthalimide, crystallised from pyridine in yellow needles, m. p. 176° (Found : N, 6·7. $C_{25}H_{18}O_6N_2$ requires N, 6·2%).

7-*Keto*-2 : 3 : 5 : 6-*dibenzo*-7 : 8-*dihydro*-1 : 8-*naphthyridine* (III).—A mixture of *o*-nitrobenzylidenehomophthalimide (II) (15 g.), stannous chloride (40 g.), and ethyl alcohol (200 c.c.) was saturated with hydrogen chloride and heated on the water-bath for 12 hours. After cooling, the tin double compound was collected, digested with excess of potassium hydroxide solution for ½ hour, cooled, and the bright yellow *potassium* salt decomposed by trituration with dilute hydrochloric acid; the resulting *ketodibenzodihydronaphthyridine* was recrystallised from glacial acetic acid, forming very pale yellow needles (12 g.), m. p. 246—247° (Found : C, 77·9; H, 4·1; N, 11·1. $C_{16}H_{10}ON_2$ requires C, 78·0; H, 4·1; N, 11·4%). It is almost insoluble in water, ether, alcohol, acetone, or benzene, slightly soluble in hot chloroform, and soluble in hot glacial acetic acid or pyridine. It dissolves in concentrated hydrochloric acid, but is reprecipitated on dilution. The potassium salt is almost insoluble in water. The *sodium* salt is slightly soluble in hot water, from which it separates in glistening, bright yellow plates (Found : Na, 8·7. $C_{16}H_9ON_2Na$ requires Na, 8·6%); it is also obtained by boiling the ketodibenzodihydronaphthyridine (III) with methyl-alcoholic sodium hydroxide, no further hydrolysis taking place.

7-*Keto*-8-β-*phenylethyl*-2 : 3 : 5 : 6-*dibenzo*-7 : 8-*dihydro*-1 : 8-*naphthyridine* was obtained from *o*-nitrobenzylidene-*N*-β-phenylethylhomophthalimide by reduction with stannous chloride, as described above. It crystallises from acetic acid in almost colourless needles, m. p. 220° (Found : C, 82·1; H, 5·2. $C_{24}H_{18}ON_2$ requires C, 82·3; H, 5·1%). It is a very weak base, and shows no acidic properties. 7-*Keto*-8-β-*piperonylethyl*-2 : 3 : 5 : 6-*dibenzo*-7 : 8-*dihydro*-1 : 8-*naphthyridine* crystallises from glacial acetic acid in pale yellow needles, m. p. 217° (Found : C, 76·0; H, 4·9. $C_{25}H_{18}O_3N_2$ requires C, 76·1; H, 4·6%).

7-*Keto*-2 : 3 : 5 : 6-*dibenzo*-1 : 4 : 7 : 8 : 9 : 10-*hexahydro*-1 : 8-*naphthyridine* (IV).—*o*-Nitrobenzylidenehomophthalimide (6 g.) or ketodibenzodihydronaphthyridine (III) (6 g.) was dissolved in glacial acetic acid (100 c.c.), saturated with hydrogen chloride, and heated with a large excess of zinc dust for 3 hours on the water-bath. The mixture was diluted with water, made strongly alkaline with ammonia, extracted with chloroform, the solvent removed, and the residue crystallised first from boiling ethyl alcohol and then from methyl ethyl ketone, colourless needles (0·5 g.), m. p. 250°, being obtained (Found: C, 77·4; H, 5·7. $C_{16}H_{14}ON_2$ requires C, 76·8; H, 5·6%). This substance (IV) is more soluble in organic solvents than the dihydrocompound (III). It is insoluble in sodium hydroxide solution, but dissolves in dilute hydrochloric acid; on concentration the *monohydrochloride* separates in colourless needles, which darken at about 225° and decompose at 270° (Found: Cl, 12·3. $C_{16}H_{15}ON_2Cl$ requires Cl, 12·5%). When its solution in dilute hydrochloric acid was treated with sodium nitrite an amorphous *nitrosoamine* gradually separated. This was extracted with chloroform, the extract washed thoroughly with sodium bicarbonate solution, and the solvent removed; the residue gave Liebermann's test for nitrosoamines. The *picrate*, prepared in alcoholic solution, crystallised from glacial acetic acid in small, yellow needles, m. p. 270° (Found: N, 14·6. $C_{22}H_{17}O_8N_5$ requires N, 14·6%).

7-*Keto*-8-β-*phenylethyl*-2 : 3 : 5 : 6-*dibenzo*-1 : 4 : 7 : 8 : 9 : 10-*hexahydro*-1 : 8-*naphthyridine*, obtained by reducing the corresponding dihydro-compound or *o*-nitrobenzylidene-*N*-β-piperonylethylhomophthalimide with zinc dust, as described above, crystallises from ethyl alcohol in colourless needles, m. p. 217° (Found: C, 81·1; H, 6·4. $C_{24}H_{22}ON_2$ requires C, 81·3; H, 6·2%). 7-*Keto*-8-β-*piperonylethyl*-2 : 3 : 5 : 6-*dibenzo*-1 : 4 : 7 : 8 : 9 : 10-*hexahydro*-1 : 8-*naphthyridine* separates from ethyl alcohol in colourless needles, m. p. 211° (Found: C, 75·4; H, 5·7. $C_{25}H_{22}O_3N_2$ requires C, 75·4; H, 5·5%).

2 : 3 : 5 : 6-*Dibenzo*-4 : 9-*dihydro*-1 : 8-*naphthyridine* (V).—The corresponding 1 : 8-dihydroketo-compound (III; 5 g.), phosphorus pentachloride (6 g.), and phosphorus oxychloride (10 c.c.) were heated for 5 hours in a sealed tube at 180°. The oxychloride was removed under diminished pressure, and the solid residue * (7 g.) heated with red phosphorus (1·5 g.) and hydriodic acid (*d* 1·7; 30 c.c.) for 9 hours at 160—170°; the pale greenish-yellow solution, containing long, pale yellow prisms, was diluted with water, boiled, and the sparingly soluble *hydriodide* decomposed by the addition

* The chloro-derivative could not be isolated from this solid residue, as it was rapidly hydrolysed to the keto-compound (III) by water.

of a large excess of ammonia. The base was extracted with chloroform, the extract dried, the solvent removed, the residual solid dissolved in hot dilute hydrochloric acid, filtered, and cooled; the hydrochloride separated in pale orange needles, which were collected, dissolved in water, and decomposed with sodium hydroxide; the resulting yellow base crystallised from ethyl alcohol in pale yellow needles (0·9 g.), m. p. 232° (Found: C, 82·4, 82·8; H, 5·4, 5·5. $C_{16}H_{12}N_2$ requires C, 82·8; H, 5·2%). It is sparingly soluble in ether, light petroleum, or benzene, fairly soluble in hot alcohol, and readily soluble in chloroform, glacial acetic acid, or hot dilute mineral acids. Its alcoholic solutions are almost colourless, with an intense violet fluorescence. The *monohydrochloride* crystallises from water in pale yellow needles which darken at about 240° and gradually decompose at higher temperatures (Found: Cl, 12·9. $C_{16}H_{13}N_2Cl$ requires Cl, 13·3%). The base does not yield a nitrosoamine or acetyl derivative, and could not be further reduced by zinc dust and acids.

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CCCXV.—*New Reference Compounds in the Sugar Group. The Methylamides of* d-, l-, *and* i-*Dimethoxysuccinic Acids and of* l-*Arabo- and* i-*Xylo-trimethoxyglutaric Acids.*

By WALTER NORMAN HAWORTH and DAVID IDRIS JONES.

COMPARED with other groups of organic substances, the carbohydrates have hitherto been provided with few fundamental reference compounds which can serve as final standards for the complete identification of the normal and labile forms of sugars through their oxidation derivatives.

The most readily accessible oxidation derivatives of the methylated aldoses are the lactones of the corresponding acids, and most of these lactones are crystalline and give characteristic phenylhydrazides. A lactone of the δ- or amylene-oxide series can be sharply differentiated from the corresponding member of the γ- or butylene-oxide series by reason of its different rate of hydrolysis as revealed by physical methods (Drew, Goodyear, and Haworth, this vol., p. 1237; also forthcoming paper by Carter, Haworth, and Robinson).

The ultimate basis on which the constitution of each of these

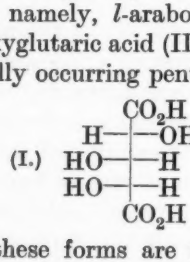
lactones rests is that of the simple dibasic acids to which they give rise on oxidation. Our further study of these lactones by methods of degradative oxidation has revealed the need of a final standard of comparison of these oxidation products with the derivatives of the stereoisomeric forms of tartaric acid and of trihydroxyglutaric acid. Methylated derivatives of these acids do not lend themselves to easy recognition. Crystalline amides of some of these acids have been prepared and examined (Hirst and Purves, J., 1923, **123**, 1352; Hirst and Robertson, J., 1925, **127**, 358) and their physical properties are of some service for the purpose of identification, but inasmuch as these amides melt with decomposition at high temperatures, their utility as standard reference substances suffers by reason of the untrustworthiness of their application in mixed m. p. determinations.

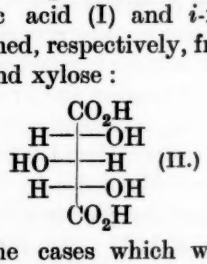
A search for new crystalline derivatives of the stereoisomeric forms of dimethoxysuccinic acid and of trimethoxyglutaric acid has led us finally to adopt as our standards the crystalline methylamides. These substances melt at a definite temperature, solidify on cooling, and then remelt at the same temperature as before, and they undergo no change either of condensation or decomposition at this elevated temperature.

Thus *l*-tartaric acid, prepared by Pasteur's method from racemic acid, was esterified to methyl *l*-tartrate, and methylation by the usual methods gave rise to *methyl* l-*dimethoxysuccinate*. The latter was converted with the aid of pure methylamine into l-*dimethoxysuccinomethylamide*. Similar methods applied to the corresponding *d*- and *i*-tartaric acids furnished the remaining stereoisomeric forms of the above methylamide. Their physical properties are tabulated below for comparison :

	M. p.	$[\alpha]_D$ in water.
d-Dimethoxysuccinomethylamide	205°	+132·6°
l- " " "	205	−131·8
i- " " "	210	Zero

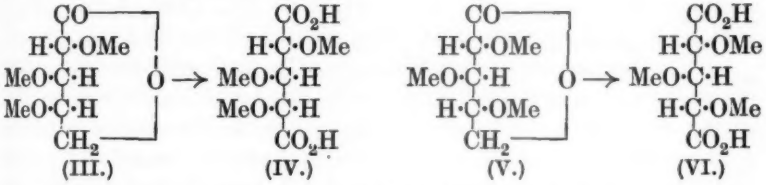
Of the four stereoisomeric forms of trihydroxyglutaric acid, two are most frequently encountered as oxidation products in the sugar group, namely, *l*-arabotrihydroxyglutaric acid (I) and *i*-xylotrihydroxyglutaric acid (II), which are obtained, respectively, from the naturally occurring pentoses, arabinose and xylose :





Both these forms are represented in the cases which we have studied. Thus, *l*-trimethyl δ-arabonolactone (III), prepared from normal methylated arabinose, has been oxidised with nitric acid and

found to give rise almost exclusively to *l*-arabotrimethoxyglutaric acid (IV). Conversion of this into the methyl ester was followed by treatment with methylamine, which gave a quantitative yield of l-*arabotrimethoxyglutaromethylamide*, m. p. 172°, $[\alpha]_D$ + 59·9°. The corresponding amide was similarly prepared. Again, the oxidation of trimethyl δ-xylonolactone (V) gave an almost quantitative yield of *i*-xylotrimethoxyglutaric acid (VI), which was converted into i-*xylotrimethoxyglutaromethylamide*, m. p. 167—168°, and also into the corresponding amide.



The isolation of these products furnishes a proof of the constitution of the two δ-lactones (III and V), and also confirms the amylene-oxide structure of the normal forms of trimethyl arabinose and trimethyl xylose.

Experimental.

d-*Dimethoxysuccinomethylamide.*—Methyl *d*-dimethoxysuccinate having $[\alpha]_D^{18°}$ + 79·9° in methyl alcohol (c = 2·04) (compare Purdie and Barbour, J., 1901, **79**, 973) was prepared from *d*-tartaric acid. The ester was dissolved in dry methyl alcohol saturated with methylamine. The solution was kept for several days, and on concentration yielded long, colourless needles which, recrystallised from light petroleum (b. p. 60—80°), had m. p. 205°; $[\alpha]_D^{15°}$ + 132·6° in water (c = 1·95); yield 90% (Found: C, 47·0; H, 7·8; N, 13·5; OMe, 29·5. $C_8H_{16}O_4N_2$ requires C, 47·05; H, 7·8; N, 13·7; OMe, 30·4%).

Methyl l-*Dimethoxysuccinate.*—A specimen of *l*-tartaric acid [m. p. 167—170°; $[\alpha]_D^{18°}$ − 14·6° in water (c = 3·15)] was prepared by fermentation methods from racemic acid, and esterified in the presence of methyl alcohol containing 3% of hydrogen chloride; yield 95%. The methyl *l*-tartrate was methylated by Purdie's reagents and gave a colourless liquid, b. p. 83°/0·07 mm.; $n_D^{18°}$ 1·4345; $[\alpha]_D^{18°}$ − 78·8° in methyl alcohol (c = 3·12) (0·2340 G. required 22·9 c.c. *N*/10-sodium hydroxide. Calc.: 22·75 c.c.) (Found: C, 46·8; H, 7·0; OMe, 58·3. Calc.: C, 46·6; H, 6·8; OMe, 60·2%).

l-*Dimethoxysuccinomethylamide.*—The methyl *l*-dimethoxysuccinate was dissolved in dry methyl alcohol, saturated with methylamine, and the solution concentrated after 40 hours; a crystalline mass then filled the containing vessel. The *methylamide* was

recrystallised from ethyl acetate; the long needles thus obtained melted at 205°, solidified on cooling, and remelted at the same temperature; $[\alpha]_D^{17°}$ — 131·8° in water (c = 1·61); yield 82% (Found: C, 46·8; H, 7·7; N, 13·8; OMe, 28·4. $C_8H_{16}O_4N_2$ requires C, 47·05; H, 7·8; N, 13·7; OMe, 30·4%).

The crystalline l-*dimethoxysuccinamide* was also made in the usual way and isolated as colourless needles which became coloured at 250°, dark at 270°, melted at 278°, and decomposed violently at 294°, a behaviour which was identical with that exhibited by the *d*-isomeride (Found: C, 40·8; H, 6·6; N, 15·8; OMe, 33·5. $C_6H_{12}O_4N_2$ requires C, 40·9; H, 6·8; N, 15·9; OMe, 35·2%).

i-*Dimethoxysuccinomethylamide.*—*meso*Tartaric acid was esterified in presence of methyl alcohol and methylated with Purdie's reagents, giving flat plates, m. p. 68°. This specimen of methyl *i*-dimethoxysuccinate was dissolved in methyl alcohol, saturated with methylamine, and the solution kept for 3 days, during which long needles separated, further crops being obtained by concentration. The *methylamide* was recrystallised from ethyl acetate; m. p. 210°; zero rotation in water (c = 1·6); yield 97% (Found: C, 46·9; H, 8·0; N, 13·6; OMe, 29·8. $C_9H_{16}O_2N_2$ requires C, 47·1; H, 7·8; N, 13·7; OMe, 30·4%).

Oxidation of Trimethyl δ-Xylonolactone.—A specimen of this lactone, m. p. 55° (Haworth and Westgarth, J., 1926, 886) was oxidised with nitric acid (d 1·42) by heating the solution in a water-bath at 70—75° for ¾ hour, and thereafter for 3 hours at 90—95°. The removal of the nitric acid was effected in the usual way and the syrupy oxidation product collected, esterified with dry methyl alcohol containing 4% hydrogen chloride, the solution neutralised with silver carbonate, and the solvent evaporated. The liquid product was dissolved in ether, dried, and distilled; b. p. 102—104°/0·09 mm.; n_D 1·4402; the yield was quantitative. That this product was methyl *i*-trimethoxyglutarate was shown by conversion into the crystalline amide (yield over 60%); the crystals turned slightly brown at 195° and melted quickly at 195—198° to a blue liquid. The rotation was zero. Comparison with an authentic specimen of *i*-xylotrimethoxyglutaramide proved its identity.

i-*Trimethoxyglutaromethylamide.* — The above ester was dissolved in methyl alcohol, saturated with methylamine, and kept for 15 hours; crystals then separated, and further crops were obtained by concentration of the solution. The *methylamide* crystallised from ethyl acetate in silky needles, m. p. 167—168°, solidifying and then remelting at 167° (yield 85%). The rotation was zero (Found: C, 48·4; H, 8·4; N, 10·85; OMe, 36·3. $C_{10}H_{20}O_5N_2$ requires C, 48·35; H, 8·1; N, 11·2; OMe, 36·4%).

Oxidation of Trimethyl δ-Arabonolactone.—This lactone (m. p. 45°; $[\alpha]_D^{21^\circ}$ + 179·5° in water) was prepared from crystalline trimethyl β-methylarabinoside as described by Drew and Haworth (this vol., p. 778). The lactone (5 g.) was dissolved in 40 c.c. of nitric acid (*d* 1·42), and the solution heated on the water-bath. The oxidation commenced at 90°, and during a period of 5 hours the evolution of brown fumes was continuous; the reaction then ceased. The nitric acid was removed by dilution with water followed by continuous distillation of the dilute acid at 40°/15 mm.; methyl alcohol was added to, and distilled from, the residue, and the resulting syrup was digested with a solution containing 80 c.c. of methyl-alcoholic hydrogen chloride (3%). Thereafter, the mineral acid was removed by neutralisation with silver carbonate, and the product, a pale yellow syrup (5·8 g.), was distilled, b. p. 105°/0·14 mm.; $n_D^{15^\circ}$ 1·4365; yield 5·25 g. The methyl trimethoxyglutarate showed $[\alpha]_D^{20^\circ}$ + 37·6° in water (c = 2·52) and $[\alpha]_D^{18^\circ}$ + 41·2° in methyl alcohol (c = 1·31) (Found: C, 47·6; H, 7·3; OMe, 58·35. Calc.: C, 48·0; H, 7·2; OMe, 62·0%). This product (0·5 g.) was dissolved in dry methyl alcohol (6 c.c.), and the solution saturated with dry ammonia. On keeping, a crystalline amide separated, (yield 0·4 g.), m. p. 228—229°. Recrystallisation from methyl alcohol raised the m. p. to 230° (decomp.) (Found: C, 43·7; H, 7·2; N, 13·0; OMe, 40·6%).

l-*Arabotrimethoxyglutaromethylamide.*—Another specimen (0·46 g.) of the preceding ester was dissolved in methyl alcohol (6 c.c.) and saturated with methylamine. After keeping for 3 days at the ordinary temperature the solution was concentrated under diminished pressure and gave crystals (yield 0·45 g.) of the *methylamide*. Recrystallisation from ethyl acetate gave radiating needles (m. p. 172°), solidifying on cooling and remelting at the same temperature; $[\alpha]_D^{18^\circ}$ + 59·9° in water (c = 1) (Found: C, 48·3; H, 8·2; N, 10·9; OMe, 35·6. $C_{10}H_{20}O_5N_2$ requires C, 48·35; H, 8·1; N, 11·2; OMe, 36·4%).

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CCCXVI.—*The Photochemical Oxidation of Alcohols by the Dichromate Ion.*

By EDMUND JOHN BOWEN and CHARLES WILLIAM BUNN.

THE photochemical oxidation of alcohols by the dichromate ion has been studied by Plotnikov (*Z. wiss. Phot.*, 1919, **19**, 40; *Z. Elektrochem.*, 1926, **32**, 13). The aim of the present work was to

obtain measurements under as great a variety of conditions as possible, and to make measurements of the quantum efficiency.

Four lamps were used for different parts of the work : a 1000-c.p. Pointolite lamp, a 1000-watt tungsten-filament lamp, water-cooled, and two quartz–mercury lamps. Copper sulphate solution filters were used to remove infra-red and red radiation, and with the mercury lamps practically monochromatic radiation was obtained with Chance's black glass and cupriammonium sulphate filters.

The reactions were carried out in small quartz cells with plane-polished quartz ends fused on, the cells being fixed in a water thermostat electrically controlled. The energies of the radiations and the absorptions of the solutions were measured with a Moll thermopile calibrated in the usual way with a Hefner lamp.

The following two points were established in the first part of the work : (*a*) The chromate ion in neutral or alkaline solution is photochemically quite insensitive towards the alcohols. The results of Plotnikov (*loc. cit.*), that ammonium chromate is photoactive, are to be explained by partial hydrolysis to dichromate.

(*b*) The photochemical reaction between acid dichromate-ion solutions and alcohols leads to aldehyde formation without deposition of a precipitate. (In neutral solutions a precipitate is thrown down.) A series of measurements made with methyl alcohol solutions showed that the photochemical reaction curve obtained from the estimation of formaldehyde by the method of Schulek (*Ber.*, 1925, **58**, 732) was consistently 20% lower than that obtained from the decrease in dichromate-ion concentration. This was shown experimentally to be due to further oxidation of the formaldehyde, and the photochemical reaction may be represented :

$$Cr_2O_7'' + 8H^{\cdot} + 3CH_3{\cdot}OH \longrightarrow 3CH_2O + 2Cr''' + 7H_2O.$$

In later experiments, the reaction was followed only by estimation of the dichromate-ion concentration, potassium iodide being added and the iodine titrated. The thermal reaction was followed at the same temperature, the reactants being contained in a blackened flask, and the true photochemical change was obtained by subtraction of the (small) thermal rate from the total rate in light.

The results of numerous experiments are summarised as follows. The quantum efficiency is independent of the following four factors : (1) light intensity, over a range of 1 : 80; (2) added acid, above a certain limit; (3) dichromate-ion concentration, between $N/10$ and $N/100$; and (4) temperature, between 15° and 50°.

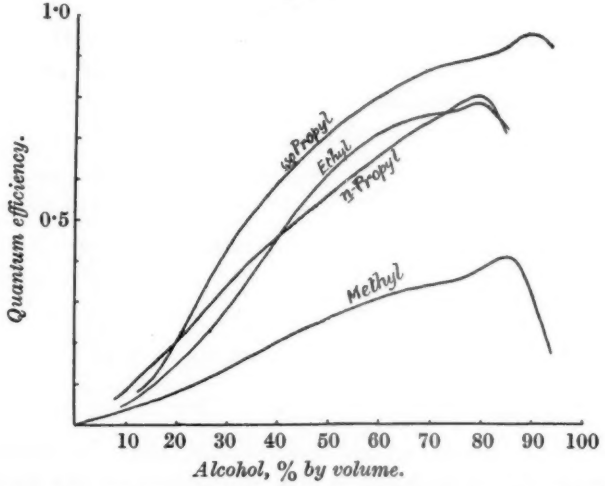
The photochemical reaction curves were determined for a series of alcohol–water mixtures at 15°, the dichromate-ion concentration being maintained at $N/20$ in each mixture, and the acid at $0{\cdot}2N$.

All the curves were linear over a large range of the first part of the reaction, and the slope gave the photochemical rates for the mixtures; these are summarised in Table I, the rates being expressed as the ratio of Cr_2O_7'' ions reduced to quanta absorbed, and plotted in Fig. 1.

TABLE I.

Methyl alcohol.		Ethyl alcohol.		*n*-Propyl alcohol.		*iso*Propyl alcohol.	
Alcohol, % by vol.	Photochemical rate.	Alcohol, % by vol.	Photochemical rate.	Alcohol, % by vol.	Photochemical rate.	Alcohol, % by vol.	Photochemical rate.
10	0·037	10	0·043	10	0·081	15	0·108
20	0·073	20	0·152	15	0·138	30	0·434
30	0·129	30	0·259	30	0·384	50	0·693
40	0·191	40	0·467	40	0·449	70	0·854
50	0·252	50	0·613	50	0·601	80	0·896
60	0·316	60	0·706	60	0·620	85	0·917
70	0·333	70	0·747	70	0·732	89	0·940
75	0·345	75	0·756	80	0·780	94	0·918
80	0·379	80	0·771	85	0·705		
85	0·400	85	0·714	89	0·606		
89	0·351						
94	0·162						
96	0 (fast dark reaction)						

FIG. 1.



As a check on these measurements, which were made in the light from a tungsten-filament lamp, filtered through copper sulphate solution, the quantum efficiency for the series of alcohols at concentrations equal to that of maximum rate was measured in monochromatic light from a quartz lamp: At 3666 Å., *Q.E.* of alcohol: methyl 0·45, ethyl 0·86, *n*-propyl 0·86, *iso*propyl 1·00. At 4200 Å. (approx.), ethyl alcohol 0·89. These results agree with the previous ones within the limit of error, if account be taken of the complete

change of apparatus. The whole absorption band of the dichromate ion in the blue and violet region is therefore equally photoactive.

The variation of reaction rate with diminishing acid concentration was investigated and showed a regular decrease, but the results cannot be simply interpreted since the reaction occurs chiefly in the forward layers of the solution, producing variations in acidity throughout the cell. The reactions were also investigated in neutral solution. In this case, a precipitate is thrown down which is not chromium hydroxide, but which is capable of liberating iodine from potassium iodide. Owing to the scattering of the light by the precipitate, the rate falls off rapidly from the beginning of the exposure, and becomes zero when one-half of the total oxidising power of the dichromate solution is utilised. The simplest explanation of this is the formation of chromate:

$$Cr_2O_7'' + 3CH_3{\cdot}OH + H_2O \longrightarrow 3CH_2O + 2OH' + 2Cr(OH)_3.$$
$$2OH' + Cr_2O_7'' \longrightarrow 2CrO_4'' + H_2O.$$

The nature of the precipitate is obscure. Plotnikov has suggested that it is chromium chromate.

Owing to the falling off of the rate with time in the neutral reactions the initial rates for different alcohol–water mixtures were obtained by calculation from the curves. Table II summarises these initial rates, expressed for convenience as the ratio of rates acid/neutral for each mixture:

TABLE II.

Methyl alcohol.		Ethyl alcohol.		*n*-Propyl alcohol.	
Alcohol, % by vol.	Ratio of rates, $\frac{\text{acid}}{\text{neutral}}$	Alcohol, % by vol.	Ratio of rates, $\frac{\text{acid}}{\text{neutral}}$	Alcohol, % by vol.	Ratio of rates, $\frac{\text{acid}}{\text{neutral}}$
30	2·77	20	2·06	15	2·2
50	2·92	30	2·15	30	2·87
70	2·80	40	2·85	50	3·3
80	2·93	50	3·1	70	3·28
82·5	2·89	70	3·2	80	3·08
85	2·62				
87·5	2·50				
90	3·0				

These measurements are not so accurate as those for acid solutions because of the uncertainty in the estimation of the initial rate. Since the ratio is practically constant, the curves for the neutral reactions are almost identical with those for the acid solutions except that the scale is about one-third. It seems that, whatever are the causes of the change in quantum efficiency with alcohol concentration, the same factors operate in acid and neutral solution.

Discussion of Results.

The results for acid solutions seem to point to the conclusion that the true quantum efficiency of the photochemical process is

the decomposition of one dichromate ion and the oxidation of 3 molecules of alcohol per quantum absorbed. The measured quantum efficiency never reaches its true value because disturbing factors cause its diminution in mixtures containing excess of either alcohol or water. The diminution at high alcohol concentrations may be due to the appearance of a new substance, such as an alkyl chromate, since here the thermal reaction becomes very fast. If this is a correct deduction, it is improbable that the reaction really consists of the simultaneous collision of 3 alcohol molecules with an activated dichromate ion; and the simplest assumption is that the real photoactive substance is an alcoholated dichromate ion, *i.e.*, an ion with alcohol molecules attached by co-ordinate links. The diminution on the low alcohol concentration side would then be due to the equilibrium between non-photoactive hydrated dichromate ions and the photoactive alcoholated ions.

Applying the mass law as an approximation for the formation of a hydrate and an alcoholate, we have :

$$\frac{(Cr_2O_7)(H_2O)^n}{(Cr_2O_7,nH_2O)} = K_1; \quad \frac{(Cr_2O_7)(ROH)^m}{(Cr_2O_7,mROH)} = K_2.$$

Putting, for simplicity, $n = m$,

$$\frac{\text{Mol. fraction } H_2O}{\text{Mol. fraction ROH}} \times \sqrt[n]{\frac{(\text{alcoholate})}{(\text{hydrate})}} = K,$$

or roughly, at low alcohol concentrations :

$$\frac{\text{Mol. fraction } H_2O}{\text{Mol. fraction ROH}} \times \sqrt[n]{\text{Quantum efficiency}} = K.$$

The following calculations from the experimental data show that $n = 1$ approximately :

Methyl alcohol.		Ethyl alcohol.	
Alcohol, mols./l.	Mol. fraction H_2O/ROH × (quantum efficiency).	Alcohol, mols./l.	Mol. fraction H_2O/ROH × (quantum efficiency).
5·5	7·4	3·3	14
11	6·5	7·1	20
16	6·8	11·4	21
23	6·4	16·9	23
31	5·6	23·6	18

n-Propyl alcohol.		*iso*Propyl alcohol.	
Alcohol, mols./l.	Mol. fraction H_2O/ROH × (quantum efficiency).	Alcohol, mols./l.	Mol. fraction H_2O/ROH × (quantum efficiency).
3	25	4	26
4·5	29	9·2	43
9·5	35	19·4	27·6
14	28		
19·4	24		

In order to make the hypothesis fit the measurements, therefore, it must be assumed that only one molecule of alcohol or water is attached to each dichromate ion. It is hardly possible to accept this result, as it does not remove the difficulty of the oxidation of 3 molecules of alcohol per quantum absorbed.

An alternative hypothesis is that the activated dichromate ions have a mean "life" and only react if they collide with alcohol molecules during this "life." Applying an approximate equation (Grüss, *Z. Elektrochem.*, 1923, **29**, 144),

$$\text{Quantum efficiency} = 4\pi\sigma^2 nct/3v,$$

where v = number of volumes of solution containing one volume of alcohol; n = number of molecules in 1 c.c.; $\sigma = 10^{-8}$ cm.; c = velocity of dichromate ion; t = "life" of activated dichromate ion.

It is significant from the point of view of this hypothesis that the quantum efficiency for all the alcohols is approximately halved at a dilution of 1 : 3; whence $t = 3 \times 10^{-11}$ second.

This time is of the order of that required for an electron shift in a molecule, and is much shorter than the life of the activated molecules of chlorine (Grüss, *loc. cit.*) and iodine (Briers, Chapman, and Walters, J., 1926, 562). The result is not improbable, because the long life of activated halogen molecules may represent the time of recombination of atoms formed after activation. No dissociation of this kind is to be expected with the dichromate ion. The mechanism of the reaction, however, must still be considered to be very imperfectly understood.

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CCCXVII.—*Equilibrium in the Systems* $MnSO_4$–K_2SO_4–H_2O *and* $MnSO_4$–$(NH_4)_2SO_4$–H_2O *at* 0°; *also in the System* $CuSO_4$–Na_2SO_4–H_2O *at* 0°, 25°, *and* 37·5°.

By ROBERT MARTIN CAVEN and WILLIAM JOHNSTON.

THE authors have previously shown (J., 1926, 2628), from an investigation of the system $MnSO_4$–K_2SO_4–H_2O at 25°, that at this temperature the double salt is tetrahydrated ($MnSO_4,K_2SO_4,4H_2O$). Since manganese sulphate itself crystallises with $4H_2O$ at 25°, and with $7H_2O$ at 0°, it was decided to investigate the hydration of its potassium double salt at 0°, in the expectation that it might

then be hexahydrated, and thus conform to the general type: $M''SO_4,M'_2SO_4,6H_2O$. Moreover, since manganese ammonium sulphate conforms to this general type, even at 25°, it was decided also to investigate the system $MnSO_4$–$(NH_4)_2SO_4$–H_2O at 0°, and thus to compare the kinds of isotherm obtained in the two cases. Further, this system was investigated at 25° by Schreinemakers (*Chem. Weekblad*, 1909, **6**, 131), and in the present paper his results are compared with those obtained by the authors (*loc. cit.*) for the system $MnSO_4$–K_2SO_4–H_2O at the same temperature.

Also, in order to study the influence of the water of crystallisation of the double salt on the type of isotherm obtained, it was decided to investigate the system $CuSO_4$–Na_2SO_4–H_2O at various temperatures, the double salt in this case always crystallising with $2H_2O$. This system has already been studied by several workers. Diacon (*Jahresber.*, 1866, 61) investigated it at 0°, and his results show that the double salt $CuSO_4,Na_2SO_4,2H_2O$ does not exist at this temperature in contact with solutions of its component salts. Nevertheless, the continuous increase in solubility of each of the two single salts caused by addition of the other salt up to the triple point indicates the presence of a considerable amount of the double salt or its ions in solution. Koppel (*Z. physikal. Chem.*, 1903, **42**, 1) showed that below 16·7° the double salt does not crystallise from a solution of its component salts; and from his results he drew a series of isotherms, showing an increased range of double salt formation above this temperature, which do not seem to be justified. Moreover, these hypothetical isotherms indicate that, from 0° to about 30°, whilst the solubility of sodium sulphate is increased by the addition of copper sulphate, that of copper sulphate is decreased by the addition of sodium sulphate. This conclusion contradicts Diacon's results at 0°. Massink investigated the same system at 20° (*Z. physikal. Chem.*, 1916, **92**, 351),* and showed a short range of double salt formation, with continuous increase of solubility of each of the single salts on addition of the other, up to the corresponding triple point. He gave, however, only one point within the double-salt range.

In view, therefore, of the conflicting and inadequate results of previous workers, the authors felt justified in investigating this system at 0° and 25°; and, since sodium sulphate is decahydrated below 33° and anhydrous above that temperature, they also decided to investigate the system above 33° (at 37·5°), to discover what

* According to an abstract of this paper (*Chem. Weekblad*, 1917, **14**, 756), Massink also investigated the system at 35°. Reference to the original paper shows that 35° is mentioned, but that the results supposed to be obtained at that temperature are missing.

influence the change in hydration of sodium sulphate had upon the isotherm.

Experimental.

The Systems $MnSO_4$–K_2SO_4–H_2O *and* $MnSO_4$–$(NH_4)_2SO_4$–H_2O *at* 0°.

For the manganese–potassium system, solutions of the two salts were made at atmospheric temperature, and various proportions of these solutions were placed successively in a flask, fitted with a stirrer, and kept immersed in a mixture of ice and water. The mixtures were stirred for 3 days before portions of the solutions were separated and analysed. The manganese was estimated volumetrically by the Volhard method, the total sulphate determined, and the potassium sulphate calculated. The same procedure was carried out with the manganese–ammonium system, except that, as the solid phases are known, they were not analysed. The ammonia and total sulphate were determined.

In Table I, the results for the manganese–potassium system at 0° are expressed as g. per 100 g. of solution or of moist solid, and the triangular diagram is used to determine the composition of the double salt (Fig. 1). In Table II, the same results, and those for the manganese–ammonium system at 0°, are expressed as mols. per 1000 g. of water; and these results are then compared graphically by means of rectangular co-ordinates with those previously obtained by Schreinemakers and the authors at 25° (Figs. 2 and 3).

The System $CuSO_4$–Na_2SO_4–H_2O *at* 0°, 25°, *and* 37·5°.

For this system at 0°, the procedure was as above, although only the liquid phases were analysed. Copper was estimated iodometrically, and total sulphate determined. For the systems at 25° and 37·5°, solutions of the two salts were made at temperatures about 15° above those required, and various proportions of the two solutions were placed in a flask, fitted with a stirrer, and kept in a thermostat at 25° $\pm$ 0·1° or 37·5° $\pm$ 0·1°. The solutions were stirred for 3 days before portions were separated and analysed. The results are expressed in Table III, and in Fig. 4 by means of rectangular co-ordinates, those of Diacon and Massink being also included in the same figure.

Conclusions.

Manganese Double Sulphates.—The following points arise :

1. Manganese potassium sulphate crystallises at 0°, as well as at 25°, with $4H_2O$.

2. Its isotherm at 0° resembles the corresponding isotherm at 25°, except that it shows a more rapid increase in solubility of

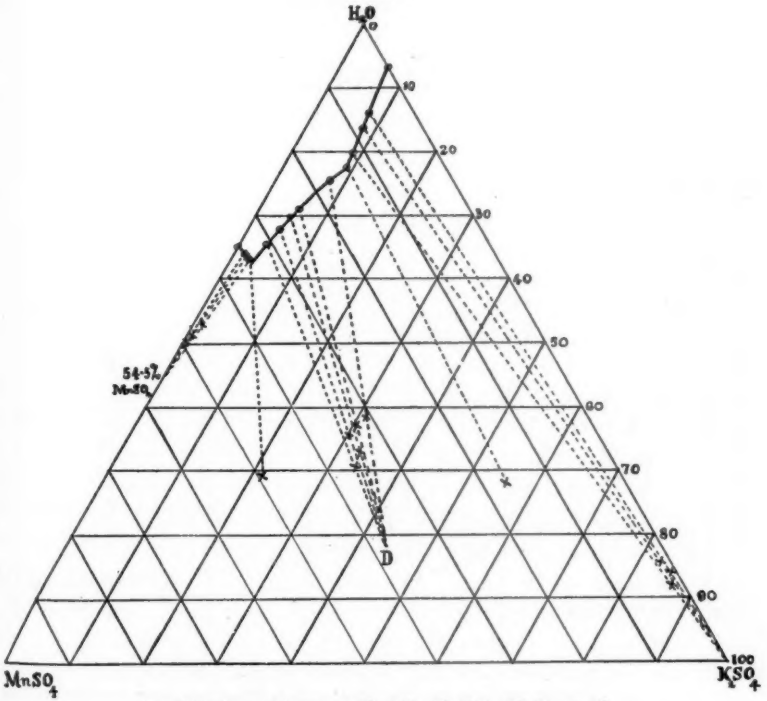
TABLE I.

The System $MnSO_4$–K_2SO_4–H_2O *at* 0°.

D.S. = Double salt.

Solutions.			Moist solids.			
K_2SO_4.	$MnSO_4$.	H_2O.	K_2SO_4.	$MnSO_4$.	H_2O.	Solid phase.
—	34·78	65·22	—	—	—	$MnSO_4,7H_2O$.
1·68	34·49	63·83	0·42	49·31	50·27	
1·85	34·53	63·62	0·70	48·00	51·30	
2·81	34·38	62·81	1·24	45·85	52·91	
3·35	34·30	62·35	21·52	49·49	28·99	$MnSO_4,7H_2O$ and D.S.
4·00	30·28	65·72	33·46	36·00	30·54	D.S.=$MnSO_4,K_2SO_4,4H_2O$.
4·48	27·62	67·90	30·31	34·46	35·23	
5·00	25·50	69·50	32·84	34·50	32·66	
5·54	23·64	70·82	30·46	32·98	36·56	
7·69	17·39	74·92	30·82	30·60	38·58	
8·88	13·68	77·44	55·60	16·90	27·50	D.S. and K_2SO_4.
8·48	11·80	79·72	86·00	1·82	12·18	K_2SO_4.
7·97	8·21	83·82	82·81	1·52	15·67	
7·75	6·21	86·04	84·55	1·11	14·34	
6·82	—	93·18	—	—	—	

FIG. 1.



Equilibrium diagram $MnSO_4$–K_2SO_4–H_2O *at* 0°.

The composition of the double salt is shown by the co-ordinates of the point D, *at which broken lines drawn through the "rests" intersect, to be* $MnSO_4,K_2SO_4,4H_2O$. *Broken lines drawn through rests for the single salts intersect at points showing* $MnSO_4,7H_2O$ (% $MnSO_4$ = 54·5) *and* K_2SO_4 (100%).

TABLE II.

The Systems $MnSO_4$–K_2SO_4–H_2O *and* $MnSO_4$–$(NH_4)_2SO_4$–H_2O *at* 0°.

(M = Manganese sulphate; K = Potassium sulphate; A = Ammonium sulphate; D = Double salt.)

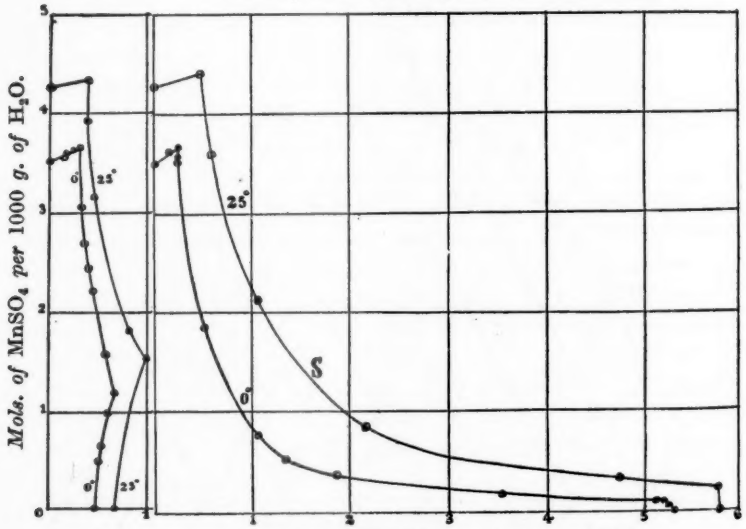
Mols. of K_2SO_4 per 1000 g. of H_2O.	Mols. of $MnSO_4$ per 1000 g. of H_2O.	Solid phase.	Mols. of $(NH_4)_2SO_4$ per 1000 g. of H_2O.	Mols. of $MnSO_4$ per 1000 g. of H_2O.	Solid phase.
—	3·533	M	—	3·533	M
0·151	3·580	M	0·168	3·623	M
0·167	3·594	M	0·251	3·665	M and D
0·257	3·624	M	0·260	3·565	D
0·308	3·642	M and D	0·261	3·525	D
0·349	3·051	D	0·531	1·868	D
0·379	2·698	D	1·069	0·769	D
0·413	2·430	D	1·315	0·531	D
0·447	2·211	D	1·864	0·377	D
0·589	1·537	D	3·551	0·167	D
0·659	1·169	D and K	3·993	0·138	D
0·611	0·978	K	5·135	0·075	D
0·546	0·649	K	5·229	0·081	D and A
0·517	0·478	K	5·254	0·017	A
0·420	—	K	5·327	—	A

FIG. 2.

A.

System $MnSO_4$–$(NH_4)_2SO_4$–H_2O *at* 0° *and* 25°.

FIG. 3.



B. *Mols. of* $(NH_4)_2SO_4$ *per* 1000 *g. of* H_2O.

S = *Curve drawn from results of Schreinemakers at* 25°.
Double salt is $MnSO_4,(NH_4)_2SO_4,6H_2O$ *at both temperatures.*

A.

System $MnSO_4$–K_2SO_4–H_2O *at* 0° *and* 25°.

B.

Mols. of K_2SO_4 *per* 1000 *g. of* H_2O.
Double salt is $MnSO_4,K_2SO_4,4H_2O$ *at both temperatures.*

TABLE III.

The System $CuSO_4$–Na_2SO_4–H_2O *at* 0°, 25°, *and* 37·5°.

(D.S. = Double salt.)

Temperature : 0°.

Mols. per 1000 g. of H_2O. $CuSO_4$.	Mols. per 1000 g. of H_2O. Na_2SO_4.	Solid phase.
—	0·387	$Na_2SO_4,10H_2O$.
0·213	0·415	
0·415	0·450	
0·590	0·468	
1·047	0·526	$Na_2SO_4,10H_2O$ + $CuSO_4,5H_2O$.
0·998	0·306	$CuSO_4,5H_2O$.
0·970	0·175	
0·929	—	

Temperature : 25°.

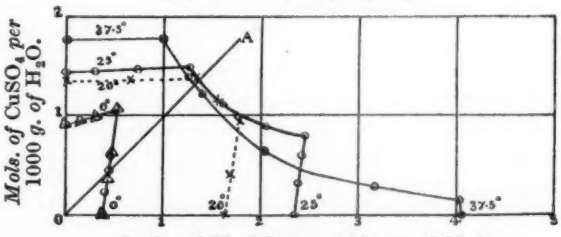
Mols. per 1000 g. of H_2O. $CuSO_4$.	Mols. per 1000 g. of H_2O. Na_2SO_4.	Solid phase.
—	2·353	$Na_2SO_4,10H_2O$.
0·256	2·394	
0·593	2·432	
0·781	2·461	$Na_2SO_4,10H_2O$ + D.S.
0·847	2·057	D.S. = $CuSO_4,Na_2SO_4,2H_2O$.
0·979	1·717	
1·068	1·603	
1·457	1·323	$CuSO_4,5H_2O$.
1·449	0·765	
1·433	0·325	
1·428	—	

Temperature : 37·5°.

Mols. of $CuSO_4$ per 1000 g. of H_2O.	Mols. of Na_2SO_4 per 1000 g. of H_2O.	Solid phase.
—	4·066	Na_2SO_4.
0·162	4·046	Na_2SO_4 + D.S.
0·280	3·183	D.S. = $CuSO_4,Na_2SO_4,2H_2O$.
0·678	2·049	
0·821	1·800	
1·209	1·406	
1·402	1·242	
1·770	1·007	D.S. + $CuSO_4,5H_2O$.
1·754	—	$CuSO_4,5H_2O$.

FIG. 4.

System $CuSO_4$–Na_2SO_4–H_2O.



Diacon's results at 0° *are indicated thus* △.
Massink's „ „ 25° „ „ „ ×, *and the isotherm by a broken line.*
OA *A line of equimolecular proportions to show solubility of double salt.*

manganese sulphate with addition of potassium sulphate up to the triple point. Some difference would be expected, since at 0° the solid phase is $MnSO_4,7H_2O$, whereas at 25° it is $MnSO_4,4H_2O$.

3. The 0°-isotherm of the potassium system differs greatly from that of the ammonium system, the range of double salt formation

in the case of the latter being much the greater. This is traceable to two factors: (*a*) the much greater solubility of ammonium sulphate, (*b*) the fact that the ammonium double salt crystallises with $6H_2O$, whereas the potassium double salt crystallises with $4H_2O$.

4. The 0°-isotherm of the ammonium system resembles the 25°-isotherm, as shown by Schreinemakers's results. Two points, however, should be noted: (*a*) The increase in solubility of manganese sulphate caused by ammonium sulphate at 25° is accentuated at 0° (compare the potassium system at 0° and 25°); (*b*) the decrease in solubility of ammonium sulphate caused by manganese sulphate at 25° is accentuated at 0°.

5. The isotherms for manganese ammonium sulphate, but not for the corresponding potassium salt, closely resemble those for the analogous copper salt (Caven and Mitchell, J., 1924, **125**, 1428).

Copper Sodium Sulphate.—A study of the results for the $CuSO_4$–Na_2SO_4–H_2O system shows a number of interesting points (see Fig. 4):

1. Diacon's results at 0° have been confirmed: there is no formation of double salt, but an increase in solubility of each single salt is caused by the presence of the other.

2. At 25°, the range of double salt formation is fairly wide. The addition of each component increases the solubility of the other up to the corresponding triple point where the double salt begins to crystallise. In the case of copper sulphate, this increase is slight but definite, in agreement with Massink's results, but in contradiction to those of Koppel.

3. At 37·5°, the range of double salt formation is greatly increased. It is to be noted, however, that although copper sulphate still shows a slight increase of solubility in presence of sodium sulphate, sodium sulphate now shows a decrease of solubility in presence of copper sulphate. A change in the form of the isotherm here is to be expected owing to the change of hydration of solid sodium sulphate.

4. The increase in range of double salt formation with rise of temperature is connected with some remarkable relationships seen when the isotherms of different temperatures are compared. Thus, although the solubilities of the single salts at 20° are less than at 25°, the double salt curve at 20°, according to Massink, appears to coincide through part of its course with the corresponding curve of the authors at 25°; and the double salt curve at 37·5°, according to the authors' results, actually falls within the corresponding curve at 25°, and even recedes from it at the sodium sulphate end because of the shortness of the solubility curve of sodium sulphate which has become anhydrous. It is evident, moreover, that the extent of the

double salt curve at 37·5° is connected with the greatly increased solubility of sodium sulphate at that temperature.

5. Thus it is concluded from the authors' results at 25° and 37·5° that the solubility of the double salt decreases with rise of temperature; and it may be supposed that the solubility at 20° is actually slightly greater than that at 25°, although Massink's result compared with the authors' does not show this.

The authors wish to thank the Governors of the Royal Technical College for a Research Assistantship which has enabled one of them (W. J.) to participate in this research.

ROYAL TECHNICAL COLLEGE, GLASGOW. [*Received, August 6th*, 1927.]

CCCXVIII.—*Complex Metallic Ammines. Part IX. The Introduction of Nitrophenol Radicals into Cobaltammine Complexes. Distinctive Behaviour of Mononitrophenoxides.*

By JAMES COOPER DUFF and EDWIN JOHN BILLS.

IN Part VIII (J., 1923, **123**, 561) it was shown that sodium salts of carboxylic acids react with aquopentamminocobaltic nitrate to give acidopentamminocobaltic salts. The sodium derivatives of several nitrophenols have now been found to react similarly with aquopentamminocobaltic nitrate and with bisaquobisethylenediamminocobaltic salts. Mono-, di-, and tri-nitrophenols have been used to examine as far as possible the influence of the number and the orientations of the nitro-groups. The unexpectedly varying nature of the series of compounds obtained is discussed below.

Previously the only nitrophenol which had been found to give cobaltammine derivatives was picric acid. Morgan and King (J., 1922, **121**, 1723) have described the reactions which occur between several cobaltammine salts and certain nitro-dyes. They found that sodium picrate reacts with aquopentamminocobaltic chloride to give aquopentamminocobaltic picrate, and suggested that nitro-dyes such as picric acid and dinitronaphthol do not, in their reactions with cobaltammines, become implicated in the cobalt complex, thus differing noticeably from the *o*-quinoneoxime (nitrosonaphthol) dyes examined similarly by Morgan and Smith (J., 1921, **119**, 704). The latter found that the quinoneoxime radical, although univalent as regards principal valency, functions as a chelate group in the complex, being linked to cobalt through a principal valency (electro-valency) and a residual valency (co-

valency). Morgan and King further suggest (*loc. cit.*) that the lack of residual valency shown by the picrate radical may be taken as evidence corroborating its *p*-quinonoid structure. In no case did they find that the picrate radical became part of the cobalt complex. It has now been found that nitrophenoxide radicals can be induced to form part of the complex, particularly in the tetrammine type. In most cases, the nitrophenoxide radicals were linked through a principal valency, but two outstanding examples have been obtained in which a complete molecule of nitrophenol appears to be implicated in the complex through residual valency.

The mononitrophenoxides have yielded results which indicate a structural difference between *m*-nitrophenol and the *o*- and *p*-isomerides, the quinone structure probably applying to the last two but not to the first. The evidence supports the views of Hantzsch (*Ber.*, 1907, **40**, 330) and of Hewitt, Johnson, and Pope (J., 1913, **103**, 1626) on these compounds.

Conductivity measurements have been used in the present work as the best method available for determining whether a nitrophenoxide radical is within the complex ion or not. It was recorded in Part VIII (*loc. cit.*) that during conductivity measurements with dilute solutions, the platinum-black of the electrodes was capable in the case of compounds of the type $[Co(NH_3)_5X]NO_3$ (X = a dibasic acid radical) of causing internal hydrolysis, changing the acido-salt into an aquo-salt. Examples of this effect have again been encountered (see Experimental), although the compounds concerned are different in type from those in Part VIII. There has also been found in the case of a *p*-nitrophenol derivative (p. 2373) an example where the platinum-black apparently induces the displacement of water from the complex by a nitrophenoxide radical. This is the only case where a fall in the value for μ has been found to occur as the result of the catalytic influence of platinum-black. It should be noted that neither type of change due to the platinum-black requires any current to be passing between the electrodes. As a further check on the value of the conductivity figures those of the corresponding sodium nitrophenoxides are given at the end of this paper.

The Pentammine Compounds.

Sodium mono- and di-nitrophenoxides form alkaline aqueous solutions which complicate the reactions with aquopentamminocobaltic nitrate. In each case there was liberation of nitrophenol and no cobaltammine compound containing *o*- or *m*-nitrophenol could be separated. The reaction in these two cases was nearly quantitatively that of the equation $[Co(NH_3)_5,H_2O](NO_3)_3 + NaO\cdot C_6H_4\cdot NO_2 = [Co(NH_3)_5(OH)](NO_3)_2 + NaNO_3 + HO\cdot C_6H_4\cdot NO_2$.

Sodium *p*-nitrophenoxide, in addition to yielding some free *p*-nitrophenol, gave a fair yield of p-*nitrophenoxopentamminocobaltic* p-*nitrophenoxide* [I; X = *p*-$C_6H_4(NO_2)\cdot O\cdot$].

$$[Co(NH_3)_5X]X_2 \qquad [Co(NH_3)_5,H_2O]X_3 \qquad \left[Co(NH_3)_5X\right]\begin{matrix}X\\OH\end{matrix}$$
(I.) (II.) (III.)

It is of interest that of the three nitrophenols only the *p*-isomeride is capable of combining with the corresponding sodium derivative; this may account for the subsequent production of a pentammino-derivative in this case, and explain the lack of success with *o*- and *m*-nitrophenols. By using the double compound of sodium *p*-nitrophenoxide and *p*-nitrophenol, a better yield of the compound (I) is obtained.

The sodium derivatives of 2 : 4- and 2 : 6-dinitrophenols gave simple aquopentammino-salts [II; X = $C_6H_3(NO_2)_2\cdot O\cdot$]. Sodium picrate yielded *picratopentamminocobaltic picrate* [I; X = $C_6H_2(NO_2)_3\cdot O\cdot$]; its relation to the aquo-picrate prepared by Morgan and King (*loc. cit.*) is considered in the experimental part. When picric acid reacts with carbonatopentamminocobaltic nitrate, two compounds can be obtained. If the carbonato-salt is used in excess, there is produced a basic salt (III), otherwise the normal compound (I) is again obtained.

The two compounds of special interest in this section are those of *p*-nitrophenol and of picric acid (III). Both these undergo a change of conductivity in the Kohlrausch cell with platinised electrodes at the ordinary temperature; this only ceases when an aquo-salt has resulted in each case:

$$[Co(NH_3)_5X]X_2 + H_2O \longrightarrow [Co(NH_3)_5,H_2O]X_3$$

Thus for the *p*-nitrophenol compound μ (for $v = 1024$) changes from 177·7 to 322·5 in 24 hours, accompanied by a colour change, while the stock solution shows but little hydrolysis after 3 months in a stoppered flask. The solutions which have been catalytically hydrolysed in the cell remain permanently hydrolysed.

The Bisethylenediammine Compounds.

The sodium derivatives of all the nitrophenols examined react with bisaquobisethylenediamminocobaltic bromide to give crystalline compounds containing nitrophenol groups. The resulting compounds showed unusual differences. Sodium picrate gave *aquopicratobisethylenediamminocobaltic picrate* (IV; X = picrate radical) and sodium 2 : 4-dinitrophenoxide gave a similar compound (as IV),

whilst the 2 : 6-isomeride yielded a basic salt (V; X = 2 : 6-dinitrophenoxide radical).

(IV.) $\left[\begin{matrix}H_2O\\X\end{matrix}Co\,en_2\right]X_2$ $\qquad\qquad$ $\left[\begin{matrix}H_2O\\X\end{matrix}Co\,en_2\right]\begin{matrix}OH\\X\end{matrix}$ (V.)

The outstanding results in this section were obtained from the mononitrophenoxides. One circumstance common to all three isomerides was that the resulting cobaltammine compounds contained a molecule of nitrophenol in addition to three nitrophenoxide radicals. The manner in which this nitrophenol molecule occurs in the compound is different in each case. Sodium *m*-nitrophenoxide produced a molecular compound between *bis*-m-*nitrophenoxobisethylenediamminocobaltic* m-*nitrophenoxide* and *m*-nitrophenol (VI; X = *m*-nitrophenoxide radical), in which the latter molecule is outside the complex.

(VI.) $[Co\,en_2\,X_2]X,HX$ $\qquad\qquad$ $\left[\begin{matrix}X\\HX\end{matrix}Co\,en_2\right]X_2$ (VII.)

From sodium *o*- and *p*-nitrophenoxides it was possible to obtain *nitrophenolnitrophenoxobisethylenediamminocobaltic nitrophenoxide* (VII; X = *o*- or *p*-nitrophenoxide radical). This is a new type of compound because the complete molecule of *o*- or *p*-nitrophenol is linked by residual valency (co-valency) in the same manner as a molecule of water in the case of aquocobaltammine salts. Formula (VII) is supported by the facts that (1) unlike all other compounds in this series, the aqueous solutions of the two salts concerned can be acidified without discharging the yellow or red colour, respectively, of the *p*- or *o*-nitrophenol compound, and (2) the aqueous solutions of these two salts when heated and then cooled and acidified have their colour discharged, yet the heating has caused no change in the values for molecular conductivity. This means that the substances hydrolyse in hot solutions, but only to the extent of having the molecule of nitrophenol displaced by a molecule of water, as in (IX):

(VIII.) $\begin{matrix}[XCo\,en_2]\,X_2\\O{=}C_6H_4{=}NO_2H\end{matrix} + H_2O \longrightarrow \left[\begin{matrix}X\\H_2O\end{matrix}Co\,en_2\right]X_2,HX.$ (IX.)

Since the molecule of nitrophenol in the complex is apparently concerned in the colour of the cold acid solution, it would appear reasonable to attribute to this complete nitrophenol molecule in the complex the corresponding *o*- or *p*-quinonoid structure (VIII), especially as the red and yellow colours of the respective compounds correspond to those of *o*- and *p*-quinones. An important point in this connexion is the fact that no free *o*-, *m*-, or *p*-nitrophenol was present at the beginning of the preparation of these compounds. The nitrophenol was liberated in each case during the reaction

between the sodium derivative and the bisaquocobaltammine salt, the probable reaction being as follows :

$$[Co\,en_2\,(H_2O)_2]Br_3 + NaO{\cdot}C_6H_4{\cdot}NO_2 \longrightarrow \left[\begin{matrix}H_2O\\HO\end{matrix}Co\,en_2\right]Br_2 + NaBr + HO{\cdot}C_6H_4{\cdot}NO_2.$$

The foregoing results suggest that whilst sodium *m*-nitrophenoxide is not quinonoid in structure, yet the *o*- and *p*-nitrophenoxides probably are; and further, when these are decomposed as in the above equation, the newly-liberated nitrophenol has the quinonoid structure and is linked up in this form in the complex in place of water.

Whilst only one cobaltammine compound of this series could be isolated from each of the *o*- and *m*-nitrophenoxides, the *p*-nitrophenoxide was found capable of producing three others in addition to (VII); by use of its addition compound with *p*-nitrophenol, $NaC_6H_4O_3N,C_6H_5O_3N,2H_2O$, two compounds represented by (IV) and (IX) were obtained by varying the conditions of reaction. In dilute aqueous solution, particularly in the presence of platinum-black, both these compounds undergo change, a nitrophenoxide radical entering the complex and displacing water :

$$\left[\begin{matrix}X\\H_2O\end{matrix}Co\,en_2\right]X_2,HX \longrightarrow [Co\,en_2\,X_2]X,HX + H_2O.$$

On attempting to recrystallise compound (IX) from hot water, some nitrophenol is liberated, yet from the solution it is possible to obtain crystals of the molecular compound *bis*-p-*nitrophenoxobisethylene-diamminocobaltic* p-*nitrophenoxide*–p-*nitrophenol* (as VI), corresponding to that obtained from *m*-nitrophenol.

Experimental.

Electrical Conductivity Measurements.—The method of measurement recorded in Part VII (J., 1922, **121**, 453) was adopted. Since most of the compounds were only moderately soluble, measurements were limited to $v = 1024$ and 2048 at 25°, at which temperature all determinations were made. Fresh solutions were made for each. The Kohlrausch cell constant was 0·2117 and the resistances measured did not greatly exceed 5000 ohms. Where conductivity changes due to the platinised electrodes were found, these were checked on new solutions. To find the extent to which change occurred it was usually necessary to leave the cell solution and the stock solution for 24 hours in the thermostat and then redetermine μ for each. No attempt was made to compare the rates at which changes occurred, as it was noted that these only took place in the neighbourhood of the electrodes. Samples of solutions which had

undergone change in this way were kept in closed tubes for 3 months and again examined. In no case had there been any tendency to revert to the original form. With unplatinised electrodes practically no catalytic effect was noticeable.

The Pentammine Series.

The Cobaltammine Reagent.—5 G. of carbonatopentamminocobaltic nitrate, 30 c.c. of water, and 20 c.c. of 2*N*-nitric acid were maintained at 45° until effervescence ceased. The solution was neutralised with 2*N*-sodium hydroxide. For the following compounds, this reagent was mixed at 45° with a solution of the corresponding sodium derivative (3 mols.) in the minimum amount of water. Except in the case of the picrate it was necessary to extract the washed precipitate with alcohol and ether to remove free nitrophenol or dinitrophenol. The product was then crystallised from water at 65°.

Sodium *o*- and *m*-nitrophenoxides produced only a precipitate of free nitrophenol. On addition of sufficient alcohol to retain this in solution, long red needles slowly separated; these were identified by analysis and reactions as hydroxopentamminocobaltic nitrate (see equation, p. 2366).

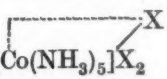
The following compounds are all easily decomposed by dilute acid or alkali. In the crystalline form and in solution, they begin to decompose at 70—80°.

p-*Nitrophenoxopentamminocobaltic* p-*nitrophenoxide* (as I; with $3H_2O$) was obtained in minute, orange, oblong plates (Found: Co, 9·34; NH_3, 13·76; nitrophenoxide, 67·8; H_2O, 8·21. $C_{18}H_{27}O_9N_8Co,3H_2O$ requires Co, 9·64; NH_3, 13·88; nitrophenoxide, 67·64; H_2O, 8·82%). By the use of the addition compound of sodium *p*-nitrophenoxide and *p*-nitrophenol, the same compound was obtained in better yield (Found: Co, 9·24; nitrophenoxide, 65·77%); $\mu_{1024} = 177·7$ and $\mu_{2048} = 189·2$; 24 hours later the cell solution had $\mu_{1024} = 322·5$ and $\mu_{2048} = 322·2$, whilst the stock solution had $\mu_{1024} = 181·2$ and $\mu_{2048} = 189·4$. The cell solution had become greenish-yellow, whilst the flask solution remained golden-yellow. The solutions were kept sealed for 3 months, and the two cell solutions then had $\mu_{1024} = 340·5$ and $\mu_{2048} = 342·8$, and the stock solutions $\mu_{1024} = 208·4$ and $\mu_{2048} = 245·3$. A few minutes in the cell caused a greater change than 3 months in the stock flask.

Aquopentamminocobaltic 2 : 4-*dinitrophenoxide* (as II; with $3H_2O$) was obtained as an orange, sandy, crystalline powder (Found: Co, 7·72; NH_3, 11·11; dinitrophenoxide, 71·88; H_2O, 8·86. $C_{18}H_{26}O_{16}N_{11}Co,3H_2O$ requires Co, 7·71; NH_3, 11·11; dinitrophenoxide, 71·76; H_2O, 9·41%); $\mu_{1024} = 284$ and $\mu_{2048} = 291·6$.

Aquopentamminocobaltic 2 : 6-*dinitrophenoxide* (as II) was obtained as an orange-red, microcrystalline powder, only sparingly soluble in water (Found : Co, 8·29; NH_3, 12·20; dinitrophenoxide, 77·68. $C_{18}H_{26}O_{16}N_{11}Co$ requires Co, 8·29; NH_3, 11·95; dinitrophenoxide, 77·21%); $\mu_{2048} = 318{\cdot}4$.

Picratopentamminocobaltic picrate (as I; with $3H_2O$) was obtained in glistening, golden leaflets (Found : Co, 6·53; NH_3, 9·53; picrate, 78·2; H_2O, 6·91. $C_{18}H_{21}O_{21}N_{14}Co,3H_2O$ requires Co, 6·68; NH_3, 9·63; picrate, 77·55; H_2O, 6·12%). The same compound resulted from the reaction between picric acid (3 mols.) and carbonatopentamminocobaltic nitrate (Found : Co, 6·35; NH_3, 9·28; picrate, 76·8%). For conductivity measurements it was difficult to obtain a solution for $v = 2048$ without heating to 60°, and this apparently caused some hydrolysis. At 25°, $\mu_{2048} = 304$, changing in the cell in 2 days to 359·1. In view of this somewhat high value for an acidopentammine salt, the compound described by Morgan and King (*loc. cit.*) was prepared and examined : at 25°, $\mu_{2048} = 288$, changing in 3 hours in the cell to 360, and over-night to 415·3, whilst the stock solution only changed to $\mu_{2048} = 299$; it was noticed that the cell solution had changed from golden-yellow to greenish-yellow. These changes suggest that Morgan and King's compound $[Co(NH_3)_5H_2O]X_3$ is not simply an aquopentammine salt, as they assert. The molecule contains $2H_2O$ less than our compound and differs in appearance, but it can be changed to our picrato-salt by crystallisation from a hot dilute solution of picric acid. A possible explanation may be that in the compound of Morgan and King one of the picrate radicals is linked to the cobalt by residual valency and to the complex by principal valency as in (X). This could account

(X.) 

for the conductivity changes and the conversion by means of picric acid into our compound.

Picratopentamminocobaltic hydroxypicrate (III; with $2H_2O$) was obtained as a brown, microcrystalline powder by stirring powdered picric acid (1 mol.) into a concentrated solution of carbonatopentamminocobaltic nitrate at 60°. The product was recrystallised from water at 60° (Found : Co, 9·09; NH_3, 13·14; picrate, 69·85; H_2O, 5·18. $C_{12}H_{20}O_{15}N_{11}Co,2H_2O$ requires Co, 9·03; NH_3, 13·02; picrate, 69·83; H_2O, 5·51%); $\mu_{2048} = 203{\cdot}3$, changing in the cell in 12 hours to 352·2, while the stock solution remained at 203·3. The cell solution changed in colour from orange to greenish-yellow. After 3 months in a sealed tube, this solution gave $\mu_{2048} = 360$, whilst the stock solution gave 225·6. When the basic picrate was

dissolved in hot dilute picric acid solution, the normal picrato-salt separated on cooling.

Bisethylenediammine Series.

The Cobaltammine Reagent.—5 G. of carbonatobisethylenediamminocobaltic bromide, 30 c.c. of water, and 20 c.c. of 2*N*-nitric acid were maintained at 50° until effervescence ceased. The solution was neutralised with 2*N*-sodium hydroxide. It was freshly made for each of the following preparations.

o-*Nitrophenol*-o-*nitrophenoxobisethylenediamminocobaltic* o-*nitrophenoxide* (as VII; with $1H_2O$) was prepared by mixing the cobaltammine reagent at 50° with 7·5 g. of sodium *o*-nitrophenoxide (3 mols.) in 70 c.c. of water. After alcohol and ether extraction, the product was crystallised from water at 70°, yielding dark red, minute, glistening plates (Found: Co, 7·83; nitrophenoxide, 73·34. $C_{28}H_{33}O_{12}N_8Co,H_2O$ requires Co, 7·86; nitrophenoxide, 73·60%). The aqueous solution is red and changes to a more scarlet tint on addition of dilute mineral acids, with separation of some nitrophenol. The acid solution becomes faintly pink on boiling. A fresh aqueous solution of the compound becomes yellow when immersed in boiling water, and subsequent addition of acid gives only the pink colour of aquocobaltammine inorganic salts. It is inferred from these reactions that a complete molecule of *o*-nitrophenol is within the complex and is only readily replaced by a molecule of water in hot solutions. Dilute alkali causes complete hydrolysis immediately. The compound is appreciably soluble in alcohol and in acetone, but not sufficiently soluble to serve for an accurate estimation of the molecular weight: values obtained ebullioscopically ranged from 780 to 900. $\mu_{1024} = 135{\cdot}6$ and $\mu_{2048} = 142{\cdot}2$. After the latter solution had been heated on the water-bath to change the colour from red to yellow, μ_{2048} became 140·2.

Bis-m-*nitrophenoxobisethylenediamminocobaltic* m-*nitrophenoxide*+ m-*nitrophenol* (as VI; with $1H_2O$) was obtained when the cobaltammine reagent at 50° was mixed with 7·5 g. of sodium *m*-nitrophenoxide in 70 c.c. of water. The mixture was filtered at 25° and the solution left over-night. The desired compound was obtained in brownish-red nodules (Found: Co, 7·81; nitrophenoxide, 72·98. $C_{28}H_{33}O_{12}N_8Co,H_2O$ requires Co, 7·86; nitrophenoxide, 73·6%). The aqueous solution is yellow and addition of dilute acid renders it pink, with liberation of all the nitrophenol; $\mu_{1024} = 75{\cdot}7$ and $\mu_{2048} = 71{\cdot}5$. The former value is high because of hydrolysis during the preparation of the solution. After this solution had been heated on the water-bath for 30 minutes, μ_{1024} became 101·5.

p-Nitrophenol was found capable of yielding the compounds A, B, C, D, as follows.

A. p-*Nitrophenol*-p-*nitrophenoxobisethylenediamminocobaltic* p-*nitrophenoxide* (as VII; with $3H_2O$). To obtain this compound it was necessary to use a solution of sodium *p*-nitrophenoxide freshly prepared from the nitrophenol: the use of the crystallised salt resulted in a mixture of A and C. The cobaltammine reagent at 50° was mixed with a solution of 6·5 g. of *p*-nitrophenol in 46·8 c.c. of *N*-sodium hydroxide and 40 c.c. of water. The precipitate, washed with alcohol and ether to remove *p*-nitrophenol, was crystallised from water at 70°. In this way, A was obtained in dark brown microcrystals which assumed a purple shade on dehydration at 90° (Found: Co, 7·30; nitrophenoxide, 69·45; H_2O, 6·72. $C_{28}H_{33}O_{12}N_8Co,3H_2O$ requires Co, 7·50; nitrophenoxide, 70·23; H_2O, 6·87%). The compound is appreciably soluble in alcohol and acetone. The aqueous solution is orange and when acidified retains a yellow colour for several minutes. If the solution is heated, then cooled and acidified, it becomes pink immediately. $\mu_{1024} = 130·2$ and $\mu_{2048} = 139·6$. After the latter solution had been heated for 15 minutes at 90° it had $\mu_{2048} = 125·7$, changing in the cell to 91·0 after 24 hours and 78·8 after 48 hours. This indicates a change from A through C into D (p. 2374). The hydrated salt changes slowly in the solid state, passing into the compound C, since after 4 months it gave aqueous solutions which at once became pink on being acidified. The anhydrous form of the salt is more stable.

B. *Aquo*-p-*nitrophenoxobisethylenediamminocobaltic* p-*nitrophenoxide* (as IV; with $2H_2O$) was obtained as a light brown, crystalline powder when the cobaltammine reagent was mixed at 70° with 15 g. of the double compound of sodium *p*-nitrophenoxide and *p*-nitrophenol in 200 c.c. of water. The precipitate was filtered immediately and free nitrophenol removed by ether extraction (Found: Co, 9·14; nitrophenoxide, 63·83. $C_{22}H_{30}O_{10}N_7Co,2H_2O$ requires Co, 9·11; nitrophenoxide, 63·98%). An aqueous solution is immediately decomposed by dilute acid, a distinction from A. On heating to 80°, the aqueous solution decomposes with separation of *p*-nitrophenol, yet the impure crystals which separate on cooling contain more than three equivalents of nitrophenoxide. There is evidently a tendency for B to pass into the more stable compound C. $\mu_{1024} = 115·8$ and $\mu_{2048} = 122·8$; the latter changes in the cell to 84·3.

C. *Aquo*-p-*nitrophenoxobisethylenediamminocobaltic* p-*nitrophenoxide* + p-*nitrophenol* (as IX; with $1H_2O$) was obtained in orange-brown microcrystals by mixing the cobaltammine reagent with 15 g. of the double sodium salt in 200 c.c. of water at 40°, filtering the solution after 2 hours, and removing free *p*-nitrophenol by ether

extraction (Found: Co, 7·74; nitrophenoxide, 71·34; H_2O, 3·8. $C_{28}H_{35}O_{13}N_8Co,H_2O$ requires Co, 7·68; nitrophenoxide, 71·87; H_2O, 4·68%). In solution, C behaves similarly to B. $\mu_{1024} = 119·5$ and $\mu_{2048} = 118·8$; after 24 hours in the cell $\mu_{2048} = 70·1$ while the stock solution gave $\mu_{2048} = 117·9$. The results support the change of C into D as below.

D. *Bis*-p-*nitrophenoxobisethylenediamminocobaltic* p-*nitrophenoxide* + p-*nitrophenol* (as VI; with $2H_2O$) was obtained from C above by crystallising it from water at 70°, filtering the solution from liberated *p*-nitrophenol, and leaving it over-night; the salt separated in dark brown nodules (Found: Co, 7·73; nitrophenoxide, 71·9; H_2O, 5·23. $C_{28}H_{33}O_{12}N_8Co,2H_2O$ requires Co, 7·68; nitrophenoxide, 71·87; H_2O, 4·68%). The yellow colour of the aqueous solution is changed to pink immediately by dilute acid. $\mu_{1024} = 88·0$ and $\mu_{2048} = 70·1$; the high value for μ_{1024} is due to the fact that the solution had been prepared at 40°.

Aquo-2 : 4-*dinitrophenoxobisethylenediamminocobaltic* 2 : 4-*dinitrophenoxide* (as IV; with $1H_2O$) was prepared by mixing the cobaltammine reagent at 60° with 9·6 g. of sodium 2 : 4-dinitrophenoxide (3 mols.) in 200 c.c. of water. After being washed, finally with ether, the pure compound crystallised from water at 70° in orange-red microcrystals (Found: Co, 7·71; dinitrophenoxide, 70·55; H_2O, 4·13. $C_{22}H_{27}O_{16}N_{10}Co,H_2O$ requires Co, 7·72; dinitrophenoxide, 71·86; H_2O, 4·71%); $\mu_{2048} = 184·1$—it was necessary to warm to 60° to obtain this solution.

Aquo-2 : 6-*dinitrophenoxobisethylenediamminocobaltic hydroxy*-2 : 6-*dinitrophenoxide* (as V) was obtained in brown microcrystals by the analogous method (Found: Co, 10·02; dinitrophenoxide, 63·45. $C_{16}H_{25}O_{12}N_8Co$ requires Co, 10·17; dinitrophenoxide, 63·10%); $\mu_{2048} = 165·7$.

Aquopicratobisethylenediamminocobaltic picrate (IV; with $4H_2O$) was obtained in orange, flat needles from the cobaltammine reagent and 12 g. of sodium picrate in 200 c.c. of water by the method used for the two preceding compounds (Found: Co, 6·16; picrate, 72·7; H_2O, 9·69. $C_{22}H_{24}O_{22}N_{13}Co,4H_2O$ requires Co, 6·18; picrate, 71·77; H_2O, 9·44%). The same compound was produced by the action of excess of picric acid in solution on carbonatobisethylenediamminocobaltic bromide at 60° (Found: Co, 6·32; picrate, 70·84%); $\mu_{2048} = 251·7$, without change in the cell on standing.

Analysis.—In both series cobalt was determined directly as sulphate by heating the compounds with concentrated sulphuric acid. The nitrophenols were estimated by heating with excess of titanous chloride solution and titrating the excess with standard ferric alum solution: in the pentammine series this was done after

precipitation of cobalt with sodium hydroxide, but in the bisethylenediammine series it was necessary to let the titanous chloride reduce both the cobaltic complex and the nitrophenol and subsequently to allow for the cobalt present. No estimation of ethylenediamine was made, since all the compounds in this series were found to yield the green *trans*-dichlorobisethylenediamminocobaltic chloride on evaporation with hydrochloric acid.

As standards for the conductivity values, the following values were determined (at 25°) for the various sodium derivatives of the nitrophenols :

	μ_{1024}.	μ_{2048}.
Sodium *o*-nitrophenoxide	82·0	92·9
Sodium *m*-nitrophenoxide	82·35	92·6
Sodium *p*-nitrophenoxide	86·35	90·0
Sodium 2 : 4-dinitrophenoxide	82·6	90·6
Sodium picrate	82·6	91·6

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CCCXIX.—*The Preparation of some Nitrohydroxybenzaldehydes and the Colour Relationships of their Substituted Phenylhydrazones.*

By HERBERT HENRY HODGSON and HERBERT GREENSMITH BEARD.

MONONITRO-*m*-HYDROXYBENZALDEHYDES were first described by Tiemann and Ludwig (*Ber.*, 1882, **15**, 2043) but correctly oriented by Friedländer and Schenck (*Ber.*, 1914, **47**, 3040), whilst Friedländer and Schreiber (*Ber.*, 1895, **28**, 1382) described the mononitration of *m*-methoxybenzaldehyde, thereby completing previous work by Ulrich (*Ber.*, 1885, **18**, 2571) and Rieche (*Ber.*, 1889, **22**, 2349). Tiemann and Ludwig's α- and β-dinitro-*m*-methoxybenzaldehydes, m. p.'s 155° and 110°, respectively, have not, however, been oriented ; this problem, together with an investigation on the di- and trinitro-*m*-hydroxy- and the dinitro-*p*-hydroxy-benzaldehydes, is now dealt with.

Controlled direct dinitration of *m*-hydroxybenzaldehyde proved impracticable, the reaction products containing unchanged material and inseparable mixtures of nitro-compounds. Nitration of 6-nitro-3-hydroxybenzaldehyde gave two dinitro-products, m. p.'s 94° and 106°, whereas nitration of 2- and 4-nitro-3-hydroxybenzaldehydes gave single products melting at 94° and 106°, respectively, which must therefore be the 2 : 6- and 4 : 6-*dinitro-3-hydroxybenzaldehydes*. These could not be methylated by the ordinary methods, but a mixture of 2 : 6- and 4 : 6-*dinitro-3-methoxybenz-*

aldehydes was obtained by the dinitration of *m*-methoxybenzaldehyde at a lower temperature than that employed by Tiemann and Ludwig (*loc. cit.*), and separated by fractional crystallisation from hot benzene, in which the latter is five times more soluble than the former. Confirmation of their constitutions was obtained by nitration of the 6-, 4-, and 2-nitro-3-methoxybenzaldehydes, the first giving a mixture of two products, m. p.'s 157° and 131°, and the other two giving single products, of m. p.'s 131° and 157°, which are therefore 4 : 6- and 2 : 6-dinitro-3-methoxybenzaldehyde, respectively. Tiemann's α-compound (*loc. cit.*) is consequently the 2 : 6-dinitro-isomeride, whereas his β-compound is a mixture of this with the 4 : 6-isomeride.

All three mononitro- and both dinitro-3-hydroxybenzaldehydes give the same trinitrated product, which must therefore be the 2 : 4 : 6-*trinitro*-3-*hydroxybenzaldehyde*.

Nitration of 3-nitro-4-hydroxybenzaldehyde with pure nitric acid gives 3 : 5-*dinitro*-4-*hydroxybenzaldehyde*, but if sulphuric acid is present only picric acid is formed. It is noteworthy that the introduction of two nitro-groups into either *m*- or *p*-hydroxybenzaldehyde or their chloro-derivatives (Hodgson and Beard, J., 1926, 2030) gives products which all melt between 90° and 110°.

The facility of decomposition of the *p*-nitrophenylhydrazones of the various nitrohydroxybenzaldehydes appears to depend upon the positions of the nitro-groups in the aldehyde residue, *e.g.*, 2 : 6-dinitro-3-hydroxy- and -3-methoxybenzaldehyde-*p*-nitrophenylhydrazones explode at about 240° and 260°, respectively, whereas the 4 : 6-dinitro-isomerides are stable above 300°.

Colours and Colour-reactions.

The colours of the nitro- and *p*-bromo-phenylhydrazones of the above aldehydes, both as solids and in aqueous and alcoholic alkaline solution, are discussed in relation to positional influences.

Acidic groups in both *o*-positions to the aldehyde radical reduce the depth of colour of the solid phenylhydrazones in a similar way to that found by Chattaway and Clemo (J., 1923, **123**, 3041) for the hydrazine nucleus; thus, the phenylhydrazones of 2- and 3-nitrobenzaldehydes are respectively crimson and deep bright orange, whereas those of the corresponding dichloro-derivatives (2 : 5-dichloro-6-nitro- and -3-nitro-benzaldehydes) are orange-yellow and orange; the introduction of a *p*-nitro-group into the hydrazine nucleus causes a further reduction of colour, *e.g.*, to a pale yellow in the case of 2 : 5-dichloro-6-nitrobenzaldehyde-*p*-nitrophenylhydrazone.

The presence of the hydroxyl group modifies Chattaway and

Clemo's generalisation, for the *p*-nitrophenylhydrazone of 2-nitro-3-hydroxybenzaldehyde is much darker than that of the 6-nitro-isomeride, although the nitro-group is ortho in each case; methylation of the hydroxyl group, however, removes the disturbing effect, the *p*-bromophenylhydrazones of 2-nitro-3-hydroxy- and -3-methoxybenzaldehydes being deep nigre-brown and bright orange, respectively.

Alcoholic solutions of the hydrazones now described obey Chattaway and Clemo's generalisation. The exceptional case quoted by them—the phenylhydrazone of 2 : 5-dichloro-6-nitrobenzaldehyde—is not repeated, however, in the *p*-nitrophenylhydrazone of this aldehyde, which, instead of merely affording the magenta colour characteristic of substituted phenylhydrazones, as would be expected if the exceptional character persisted, now gives a pronounced blue colour, showing that the nitro-group in the aldehyde residue is again functioning in a quinonoid structure.

2 : 5-Dichloro-3-nitrobenzaldehydephenylhydrazone gives the pronounced brown colour with alkalis associated with Chattaway and Clemo's scheme, but the *p*-nitrophenylhydrazone gives a blue and not a magenta colour as expected.

The magenta colours given by *m*-hydroxy- and nitro-*m*-hydroxybenzaldehyde-*p*-nitrophenylhydrazones persist to much greater dilutions than if the hydroxyl group is absent, and that these colours are not due to salt formation alone is shown by the fact that the *m*-nitrophenylhydrazone of the *m*-hydroxyaldehyde gives no colour reaction.

The *p*-bromophenylhydrazones of the nitrohydroxyaldehydes are colourless in aqueous alkaline solution, thus, by contrast with the foregoing, showing that the methine group is far more resistant to quinonoid formation than the imino-group. This same difference is also illustrated by the fact that when aqueous alkaline solutions of benzaldehyde-*p*-nitrophenylhydrazone and *p*-nitrobenzaldehyde-phenylhydrazone are diluted, the colour of the former persists to much greater dilutions (about 400-fold). Differential suppression of colour is shown by the sequence of colour changes (blue, violet, magenta) on dilution of *p*-nitrobenzaldehyde-*p*-nitrophenylhydrazone.

The pronounced colour effects in alcoholic alkaline solutions when a nitro-group is in the para-position in each nucleus suggest a double quinonoid structure (*e.g.*, $OK\cdot NO{:}C_6H_4{:}C{:}N\cdot N{:}C_6H_4{:}NO\cdot OK$), since in a mixture of two singly-quinonoid compounds the magenta of the hydrazine-quinonoid compound would predominate, as it does if a *m*-hydroxyl group is present in the aldehyde nucleus.

Correction.—Hodgson and Beard (J., 1926, 2034) nitrated what was thought to be pure 4-chloro-3-hydroxybenzaldehyde and

obtained what they regarded as the 2- and 6-nitro-derivatives. It is now found that the 4-nitro-3-hydroxybenzaldehyde from which the above chloro-derivative had been prepared contained some of its 2-nitro-isomeride—these two are very difficult to separate—and consequently the resulting chloro-compound was a corresponding mixture. The supposed 4-chloro-6-nitro-3-hydroxybenzaldehyde is now shown to be the 2-nitro-isomeride (by conversion to 2 : 4-dichloro-3-hydroxybenzaldehyde), and the supposed 4-chloro-2-nitro-3-hydroxybenzaldehyde is really the 2-chloro-4-nitro-compound (identified by mixed m. p. and comparison of semicarbazones and *p*-nitrophenylhydrazones).

Experimental.

Nitration of 6-Nitro-3-hydroxybenzaldehyde.—To the aldehyde (10 g.; m. p. 166°) in glacial acetic acid (30 c.c.) solution at 70°, nitric acid (10 c.c.; *d* 1·42) was added during ¼ hour; the mixture was kept for a further ¼ hour and poured into ice water (150 c.c.); and the voluminous mass of crystals (9 g.; m. p. 71—74°) which slowly separated was extracted with boiling water, which removed 2 : 6-dinitro- from the much less soluble 4 : 6-dinitro-3-hydroxybenzaldehyde.

Nitration of 2-Nitro-3-hydroxybenzaldehyde.—2 G. on similar treatment gave only the above water-soluble product (1·8 g.), identified by a mixed m. p. determination and through the *p*-nitro- and *p*-bromo-phenylhydrazones.

Nitration of 4-Nitro-3-hydroxybenzaldehyde.—The above treatment gave unchanged material only; nitration of a sulphuric acid solution by potassium nitrate (1 mol.) gave a mixture of 4 : 6-dinitro- and 2 : 4 : 6-trinitro-3-hydroxybenzaldehydes with unchanged material, whereas excess of potassium nitrate (2 mols.) gave mainly the trinitro-product. If the finely-powdered aldehyde (10 g.) was added gradually to well-stirred synthetic nitric acid (50 g.; 98%) at 5—10°, and the mixture was allowed to attain room temperature before being poured on ice (250 g.), the trinitro-product (3 g.) separated, and the 4 : 6-dinitro-compound (5·4 g.) could be salted out of solution. Identity of the latter with the less soluble product above was established as in the case of the more soluble product.

2 : 6-*Dinitro-3-hydroxybenzaldehyde* is more soluble in the usual solvents than its 4 : 6-isomeride, and crystallises from water in colourless needles, m. p. 94° (Found: N, 13·3. $C_7H_4O_6N_2$ requires N, 13·2%). On exposure to air, it acquires a deep brown colour, whereas its alcoholic solution turns green. The yellow *sodium* and dark orange *ammonium* salts are both very soluble in water, but the silver salt could not be obtained. The p-*nitrophenylhydrazone*, deep

terra-cotta needles which explode at 240—242°, and the p-*bromophenylhydrazone*, similar crystals, m. p. 166—167° (decomp.) (Found: Br, 20·8. $C_{13}H_9O_5N_4Br$ requires Br, 21·0%), were both crystallised from glacial acetic acid.

4 : 6-*Dinitro*-3-*hydroxybenzaldehyde* crystallises from dilute acetic acid in almost colourless needles, m. p. 106° (Found: N, 12·9%). The orange *sodium* and dark orange *ammonium* salts are very soluble in water, but the silver salt could not be prepared. The p-*nitrophenylhydrazone* forms deep reddish-orange needles, which decompose slowly at 282—283°; the p-*bromophenylhydrazone* forms dark crimson needles, m. p. 249—250° (decomp.) (Found: Br, 20·8%).

2 : 4 : 6-*Trinitro*-3-*hydroxybenzaldehyde* is produced when 6-nitro-3-hydroxybenzaldehyde (10 g.) in concentrated sulphuric acid (50 g.) is treated gradually with a mixture of nitric acid (25 c.c.; *d* 1·42) and sulphuric acid (25 c.c.; *d* 1·84) at 70—75°; the cooled mixture is poured on ice (200 g.); the precipitate crystallises from benzene in stout, colourless, hexagonal prisms, m. p. 161—162° (decomp.) (Found: N, 16·7. $C_7H_3O_8N_3$ requires N, 16·3%). The product is much more soluble in water than picric acid. The solutions in alkalis are deep red, although the *sodium* salt crystallises in bright yellow needles. The p-*nitrophenylhydrazone*, dark crimson needles, exploded violently at 228—230°, and the p-*bromophenylhydrazone*, deep olive-green parallelepipeds with metallic lustre, also exploded violently at 218—220° (Found: Br, 18·8. $C_{13}H_8O_7N_5Br$ requires Br, 18·8%). The *azine* was prepared by adding a mixture of hydrazine sulphate (1 g.), sodium hydroxide (3 c.c.; 20%), and water (5 c.c.) to a hot solution of the aldehyde (2 g.) in water (60 c.c.), and separated, on cooling, in bright yellow micro-needles; it is readily soluble in acetic acid (50%) and alcohol, insoluble in benzene and chloroform, and gives red solutions with alkalis; it explodes violently at 150—160°.

2 : 4 : 6-Trinitro-3-hydroxybenzaldehyde was also obtained from 2- and 4-nitro-3-hydroxybenzaldehyde, but the product from the latter was much less pure than in the other cases.

Dinitration of p-*Hydroxybenzaldehyde*.—Mixtures of nitric and sulphuric acids yielded only picric acid, but when 3-nitro-4-hydroxybenzaldehyde (10 g.) was added with stirring to nitric acid (80 g.; 98%) at 5° and the deep red solution was allowed to warm to 10° and then poured on ice (150 g.), a mixture (10 g.) of 3 : 5-dinitro-4-hydroxybenzaldehyde and picric acid was obtained, the latter being eliminated by one crystallisation from glacial acetic acid.

3 : 5-*Dinitro*-4-*hydroxybenzaldehyde* crystallises in colourless needles, m. p. 102—103° (Found: N, 13·1. $C_7H_4O_6N_2$ requires

N, 13·2%), which are moderately soluble in water; the *sodium* salt is pale orange. The p-*nitrophenylhydrazone*, deep orange microcrystals, slowly decomposes at 283—284°; the p-*bromophenylhydrazone*, brick-red needles, decomposes rapidly at 242—244° (Found: Br, 20·9. $C_{13}H_9O_5N_4Br$ requires Br, 21·0%); the *phenylhydrazone*, deep maroon needles, has m. p. 203° (Found: N, 18·6. $C_{13}H_{10}O_5N_4$ requires N, 18·5%).

Some Hydrazones of 3-*Nitro*-4-*hydroxybenzaldehyde*.—These were all crystallised from glacial acetic acid. Phenylhydrazone: dark red needles, m. p. 175—176° (slow decomp.) (Schöpff, *Ber.*, 1891, **24**, 3776, gives m. p. 175—176°). p-*Nitrophenylhydrazone*: dull orange needles, m. p. 247—249° (decomp.) (Found: N, 18·7. $C_{13}H_{10}O_5N_4$ requires N, 18·5%). p-*Bromophenylhydrazone*: bright red needles, m. p. 192—193° (Found: Br, 23·6. $C_{13}H_{10}O_3N_3Br$ requires Br, 23·8%).

Nitration of m-*Methoxybenzaldehyde*.—(a) *Mononitration*. Friedländer and Schreiber's conditions (*loc. cit.*), together with Rieche's test (*loc. cit.*) for the end-point of mononitration, gave no solid products until the temperature was allowed to rise to 20°; 40 g. of *m*-methoxybenzaldehyde then afforded 31g. of nitrated product and 15 g. of unchanged material. By the use of 85% nitric acid, however, 30 g. of nitrated products were obtained from 25 g. of aldehyde; when this yield was dissolved in hot benzene (20 g.) 2-nitro-3-methoxybenzaldehyde (11 g.) was deposited on cooling, and the mother-liquor contained some 6-nitro-3-methoxybenzaldehyde. No 4-nitro-3-methoxybenzaldehyde was ever isolated. Tröger and Fromm's statement (*J. pr. Chem.*, 1925, **111**, 217) that the 6-nitro-isomeride is absent has been shown to be incorrect, inasmuch as 6-nitro-3-methoxybenzoic acid has been isolated after oxidation of the foregoing mixture.

(b) *Dinitration*. Tiemann and Ludwig's conditions (*loc. cit.*) gave small yields accompanied by much charring; better results were obtained as follows: *m*-Methoxybenzaldehyde (10 g.) was added gradually to a mixture of potassium nitrate (17 g.) in concentrated sulphuric acid (80 g.) at 0—5°, then poured on ice, and the resulting colourless solid (12·4 g.) was extracted twice with boiling water, which dissolved Tiemann's β-compound (3 g.; m. p. 110—130°) and left the α-compound, which was almost pure 2 : 6-dinitro-3-methoxybenzaldehyde, m. p. 156—157° after one crystallisation from benzene. The β-compound (3 g.) was dissolved in hot benzene (16 g.), which deposited only 2 : 6-dinitro-3-methoxybenzaldehyde on cooling; the mother-liquor contained chiefly the 4 : 6-dinitro-isomeride. The total yields from the above nitration were 80% of 2 : 6- and 20% of 4 : 6-dinitro-3-methoxybenzaldehydes.

Nitration of 6-*Nitro*-3-*methoxybenzaldehyde*.—The aldehyde (10 g.) was added to nitric acid (100 c.c.; 98%) at 20°, kept for ½ hour, and then poured into ice water. The colourless solid (11·5 g.) which separated was fractionally crystallised from benzene and proved to be mainly 2 : 6- (m. p. 157°) with a little 4 : 6-dinitro-3-methoxybenzaldehyde.

Nitrations of 4- *and* 2-*Nitro*-3-*methoxybenzaldehydes*.—These aldehydes (10 g. each) gave almost pure 4 : 6- (10 g.; m. p. 127—131°) and 2 : 6-dinitro-3-methoxybenzaldehydes (11·5 g.; m. p. 152—156°) which melted at 131° and 157° respectively after one crystallisation from benzene.

2 : 6-*Dinitro*-3-*methoxybenzaldehyde* crystallises from benzene in stout, hexagonal prisms, m. p. 157° (Found : N, 12·4. $C_8H_6O_6N_2$ requires N, 12·3%); 5 g. require 60 g. of boiling benzene for complete solution. The p-*nitrophenylhydrazone* forms pale orange, elongated, hexagonal plates, which explode at about 260°, and the p-*bromophenylhydrazone* terra-cotta needles, m. p. 196—197° (decomp.) (Found : Br, 20·0. $C_{14}H_{11}O_5N_4Br$ requires Br, 20·2%). On being boiled with 50 c.c. of 1% potassium permanganate solution, the aldehyde (1 g.) was oxidised to 2 : 6-*dinitro*-3-*methoxybenzoic acid*. This forms colourless needles, m. p. 199° (Found : N, 11·9. $C_8H_6O_7N_2$ requires N, 11·6%), which give a yellow solution in aqueous sodium carbonate with liberation of carbon dioxide.

4 : 6-*Dinitro*-3-*methoxybenzaldehyde* crystallises from benzene in hexagonal prisms, m. p. 131° (Found : N, 12·3. $C_8H_6O_6N_2$ requires N, 12·3%); 5 g. require 12 g. of boiling benzene for complete solution; p-*nitrophenylhydrazone*, terra-cotta needles, m. p. above 300° without explosion (Found : N, 19·5. $C_{14}H_{11}O_7N_5$ requires N, 19·4%); p-*bromophenylhydrazone*, dull red needles, m. p. 254—256° (decomp.) (Found : Br, 20·3. $C_{14}H_{11}O_5N_4Br$ requires Br, 20·2%). Oxidation as above gave 4 : 6-dinitro-3-methoxybenzoic acid, m. p. 188—189° (Giua, *Gazzetta*, 1915, **45**, 352, gives m. p. 186—187°) (Found : N, 11·8. Calc. : N, 11·6%), which liberates carbon dioxide from sodium carbonate, but much less readily than its isomeride above.

Nitration of 2 : 5-*Dichlorobenzaldehyde*.—The method of Gnehm and Banziger (*Ber.*, 1896, **29**, 876) results in 2 : 5-dichloro-6-nitrobenzaldehyde (3 parts) and a second product (1 part) which has now been diagnosed as 2 : 5-*dichloro*-3-*nitrobenzaldehyde* (by conversion into 2 : 3 : 5-trichlorobenzaldehyde); it forms a *phenylhydrazone*, orange needles, m. p. 171°, and a p-*nitrophenylhydrazone*, deep orange needles, m. p. 290—292° (decomp.). On oxidation with alkaline permanganate, 2 : 5-*dichloro*-3-*nitrobenzoic acid* results; this crystallises from glacial acetic acid in colourless needles, m. p.

220° (the 6-nitro-acid has m. p. 143—144°) (Found: Cl, 30·1. $C_7H_3O_4NCl_2$ requires Cl, 30·0%).

2 : 3 : 5-*Trichlorobenzaldehyde* is volatile in steam, has a characteristic pungent odour, is soluble in the usual organic solvents, and crystallises from dilute alcohol in colourless needles, m. p. 56° (the 2 : 4 : 5-isomeride melts at 110—111°) (Found: Cl, 50·0. $C_7H_3OCl_3$ requires Cl, 50·1%). On oxidation with neutral permanganate, 2 : 3 : 5-trichlorobenzoic acid results, m. p. 162° (Cohen and Dakin, J., 1902, **81**, 1331, give m. p. 162°).

Additional Nitrophenylhydrazones used for Comparison Purposes.—All were crystallised from glacial acetic acid. They are tabulated under the heading of the components from which they were prepared.

Benzaldehyde.	Nitrophenylhydrazine.		M. p.
3-Hydroxy-	*o*	Terra-cotta needles	195°
,,	*m*	Deep crimson needles	209—210
,,	*p*	Terra-cotta needles	219—220
6-Nitro-3-hydroxy-	*o*	Deep terra-cotta needles	248—250 (slow decomp.)
,, ,,	*m*	Scarlet needles	257—258 (slow decomp.)
6-Nitro-3-methoxy-	*p*	Terra-cotta needles	281—283
4- ,, ,,	*p*	Saffron needles	257—258
2- ,, ,,	*p*	Curly orange needles	222—223
2 : 5-Dichloro-6-nitro-	*p*	Fine pale yellow needles	269—270 (decomp.)

Additional p-*Bromophenylhydrazones.*—All were crystallised from glacial acetic acid.

Benzaldehyde.		M. p.
6-Nitro-3-hydroxy-	Reddish-brown, hexagonal clusters	214—215°
4- ,, ,,	Crimson needles	179—180
2- ,, ,,	Nigre-brown needles	194—195 (rapid decomp.)
6-Nitro-3-methoxy-	Light crimson needles	235—236
4- ,, ,,	Pale orange needles	177—178
2- ,, ,,	Orange needles	193—194

Persistence of Colour Effects on Dilution.—Test. 0·01 G. of the hydrazone was treated with 15 c.c. of alcoholic potassium hydroxide (10 g. in 75 g. of solution), and the coloured mixture then gradually diluted with water.

(a) *Nitro-group in phenylhydrazine portion only.* The intense magenta-violet colour of benzaldehyde-*p*-nitrophenylhydrazone was not dispersed until 18,000 c.c. of water had been added.

(b) *Nitro-group in aldehyde portion only.* The deep greenish-blue colour of *p*-nitrobenzaldehydephenylhydrazone required only 35 c.c. of water for its dispersion.

Colours produced by Aqueous and Alcoholic Alkalis.—Test. 0·05 G. of hydrazone was treated with 5 c.c. of 10% aqueous or alcoholic potassium hydroxide. The hydrazones are tabulated

Colours produced by Aqueous and Alcoholic Alkalis.—Test. 0·05 G. of hydrazone was treated with 5 c.c. of 10% aqueous or alcoholic potassium hydroxide. The hydrazones are tabulated as in the previous tables.

Key to abbreviations. S. = same; D. = deeper; N. = no coloration.

Benzaldehyde.	Phenylhydrazine.	Aqueous alkali. Cold.	Aqueous alkali. Hot.	Alcoholic alkali. Cold.	Alcoholic alkali. Hot.
3-Hydroxy-	*o*-Nitro-	Bordeaux.	S.	D. Bordeaux.	D.
,,	*m*- ,,	Yellow.	S.	Yellow.	S.
,,	*p*- ,,	Bordeaux.	S.	D. Bordeaux.	S.
6-Nitro-3-hydroxy-	*o*- ,,	Orange.	D.	Olive-green.	D.
,, ,,	*m*- ,,	N.	Red.	Pale olive-green	D.
,, ,,	*p*- ,,	Bordeaux.	S.	Bluish-magenta.	S.
4- ,, ,,	*p*- ,,	Bordeaux.	S.	Reddish-violet.	S.
2- ,, ,,	*p*- ,,	Bordeaux.	S.	Bluish-magenta.	S.
6-Nitro-3-methoxy-	*p*- ,,	N.	N.	Blue (trace of red).	D.
4- ,, ,,	*p*- ,,	N.	N.	Pure cobalt-blue.	S.
2- ,, ,,	*p*- ,,	N.	N.	Blue (trace of red).	S.
4 : 6-Dinitro-3-hydroxy-	*p*- ,,	Bordeaux.	S.	Reddish-violet.	S.
2 : 6- ,, ,,	*p*- ,,	Bordeaux.	S.	Violet.	D.
4 : 6-Dinitro-3-methoxy-	*p*- ,,	N.	N.	Bluish-green.	Violet.
2 : 6- ,, ,,	*p*- ,,	N.	N.	Cobalt-blue.	S.
2 : 4 : 6-Trinitro-3-hydroxy-	*p*- ,,	Instantaneous blue quickly fades, giving canary-yellow, very explosive solid (Na salt) and magenta solution.	Blue develops.	Bluish-green.	Bluish-black.
3-Nitro-4-hydroxy-	*p*- ,,	Magenta.	S.	Magenta.	S.
3 : 5-Dinitro-4-hydroxy-	*p*- ,,	Magenta.	S.	Magenta.	S.
2 : 5-Dichloro-6-nitro-	*p*- ,,	N.	N.	Blue.	D.
2 : 5-Dichloro-3-nitro-	*p*- ,,	N.	N.	Blue.	D.
6-Nitro-3-hydroxy-	*p*-Bromo-	Substance turns from reddish-brown to deep orange, but no solution effect.	S.	Yellow.	S. Green with stronger alkali.
4- ,, ,,	*p*- ,,	N.	N.	Brown.	Greenish-brown with excess.
2- ,, ,,	*p*- ,,	Substance turns crimson; solution colourless.	S.	Red solution.	Greenish-brown with excess.
6-Nitro-3-methoxy-	*p*-	N.	N.	Pale green.	D.
4- ,, ,,	*p*- ,,	N.	N.	Deep green, becoming yellow.	Bluish-green.
2- ,, ,,	*p*- ,,	N.	N.	N.	Red.
4 : 6-Dinitro-3-hydroxy-	*p*- ,,	Red.	S.	Olive-green.	D.
2 : 6- ,, ,,	*p*- ,,	Pale olive-green solution. Deep orange substance.	S.	Deep green.	S.
4 : 6-Dinitro-3-methoxy-	*p*- ,,	N.	N.	Deep blue.	S.
2 : 6- ,, ,,	*p*- ,,	N.	N.	Deep green.	D.
2 : 4 : 6-Trinitro-3-hydroxy-	*p*- ,,	Substance changes to brownish-red; colourless solution.	S.	Instantaneous bright blue.	Blue-black.
2 : 5-Dichloro-6-nitro-	Unsubstituted.	N. (cf. Chattaway).	N.	Yellow.	Reddish-brown changes to deep red and then to yellow. Colourless solid on dilution with water.
2 : 5-Dichloro-3-nitro-	,,	N.	N.	Dark brown.	D.
3-Nitro-4-hydroxy-	*p*-Bromo-	N.	S.	Red.	S.
3 : 5-Dinitro-4-hydroxy-	*p*- ,,	Substance turns brick red.	S.	Substance turns darker red.	S.
,, ,,	Unsubstituted.	N.	N.	Red.	S.

(c) *Nitro-groups in both portions.* The intense cobalt-blue colour of *p*-nitrobenzaldehyde-*p*-nitrophenylhydrazone became violet with about 25 c.c. of water, magenta with 25—50 c.c., and vanished at 275 c.c.

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TECHNICAL COLLEGE, HUDDERSFIELD. [*Received, August 6th*, 1927.]

NOTES.

The Structure of Quinizarin. By ALBERT GREEN.

Two alternative schemes were advanced (J., 1926, 1430) for the reaction between quinizarin and thionyl chloride, the second of which suggested the replacement of a carbonyl oxygen atom by two atoms of chlorine. This is now shown to be improbable, for diacetylquinizarin (4 g.), m. p. 207—208°, after boiling with an excess of thionyl chloride for 2 hours, crystallised in the polymorphic form (3·8 g.), which was free from chlorine and melted, either alone or mixed with an authentic specimen, at 200°.

Although this lack of reactivity on the part of a derivative, in which the probably mobile hydrogens of the hydroxyl groups are replaced, would appear to invalidate the second mechanism suggested for the formation of 10-chloro-1-hydroxy-4 : 9-anthraquinone from quinizarin, it should not be held to dispose of it entirely, since there are many examples of carbonyl groups in free hydroxyanthraquinones showing properties different from those they display in simple derivatives. The *meso*-carbonyl groups influence, and are influenced by, substituents in the α-positions of anthraquinones : *e.g.*, whilst anthraquinone itself yields an oxime only with difficulty, 1-chloroanthraquinone easily gives the oxime; 1-hydroxyanthraquinone cannot be oximated, yet its ethers yield monoximes (Freund and Achenbach, *Ber.*, 1910, **43**, 3251).

Whilst it is clear, therefore, that any deduction from an experimental result obtained with an alkylated or acylated hydroxyanthraquinone should be applied to the hydroxy-compound itself with caution, nevertheless the work described above strengthens the first suggestion (*loc. cit.*), that quinizarin assumes a reactive *ortho*-quinonoid state (1 : 10-dihydroxy-4 : 9-anthraquinone) when it reacts with thionyl chloride to yield 10-chloro-1-hydroxy-4 : 9-anthraquinone. Furthermore, in this reaction only one of the hydroxyl groups is affected, and this affords experimental support

for the suggestion of Perkin (J., 1899, **75**, 433) that, although the two hydroxyls of quinizarin, under suitable conditions, may assume a double quinonoid change, in the case of the second hydroxyl group this change is not readily achieved and is of an unstable nature.

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Solubility of Cupric Sulphide in Alkali Sulphides in Presence of Sulpharsenates. By CHRISTINA DAVIES and ALEXANDER DONALD MONRO.

ALTHOUGH the slight solubility of cupric sulphide in yellow ammonium sulphide is well known, the enhanced solubility in presence of metals of the arsenic group has been little studied. Wohler (*Annalen*, 1840, **34**, 236) and Storch (*Ber.*, 1883, **16**, 2015) have shown that the sulpho-salts of these acids promote the solubility of cupric sulphide, but as no quantitative data were available a further study of the Cu–As system was made.

Solutions of various quantities of arsenic trioxide in hydrochloric acid were diluted and to each was added a solution containing 0·200 g. of copper. The mixture was completely precipitated as sulphide, which was filtered off, washed, and warmed with 50 c.c. of yellow ammonium sulphide [78·47 g. of sulphur and 73·26 g. of ammonia per litre, *i.e.*, approximately $(NH_4)_2S_2$]. The resulting mixture was filtered, and the filtrate treated with hydrochloric acid to precipitate copper and arsenic sulphides. After another filtration the precipitate was treated with warm dilute nitric acid to separate the copper, which, after evaporation with sulphuric acid, was precipitated and weighed as thiocyanate. The following results were obtained :

As present (mg.) ...	0	83·3	113·6	253·2	254·5	265·2	349·7	613·5
Cu dissolved (mg.)..	7·8	29·5	34·5	52·0	52·2	53·0	61·0	80·4

The amount of copper dissolved rises steadily with increasing amounts of arsenic until it becomes ten times its original value. This agrees with our observation that it is possible for small amounts of copper in copper–arsenic mixtures to be entirely missed in a qualitative analysis, unless the arsenic group is examined for copper.

A second series was tried in which colourless ammonium sulphide was substituted for yellow ammonium sulphide. No copper was found in the arsenic filtrate. Pure sodium sulphide gave irregular results. With 0·1600 g. of arsenic, 0·0373 g. of copper appeared

in the filtrates, but although two other results gave appreciable dissolved copper, other experiments gave negative results. Qualitative experiments showed that copper sulphide dissolved appreciably in presence of arsenic sulphide, giving unstable solutions from which cupric sulphide was reprecipitated on warming.

A solution of sodium polysulphide (16 g. of sulphur and 120 g. of $Na_2S,9H_2O$ per litre, *i.e.*, Na_2S_2) gave stable solutions containing arsenic and copper. The influence of arsenic was not so great as in the first series of experiments, but was by no means negligible. The results were as follows :

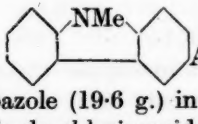
Cu taken, 0·200 g.; 50 c.c. of Na_2S_2 solution.

As (mg.)	0	149·2	237·7	365·5	480·0	620·2
Cu diss. (mg.).....	41·8	48·5	50·7	51·8	52·0	53·0

—UNIVERSITY OF GLASGOW. [*Received, June 25th,* 1927.]

9-*Methylcarbazole*-3-*arsinic Acid and its Reduction Products.* By HAROLD BURTON and CHARLES STANLEY GIBSON.

3-AMINO-9-METHYLCARBAZOLE was prepared from 9-methylcarbazole (Burton and Gibson, J., 1924, **125**, 2501) by nitration in acetic acid solution and reduction of the 3-nitro-9-methylcarbazole by means of tin and hydrochloric acid (Lindemann, *Ber.*, 1924, **57**, 555; Morgan and Read, J., 1922, **121**, 2715). It was characterised by its m. p., 173—174°, and by its acetyl derivative, m. p. 208—209° (Found : C, 75·65; H, 5·65. Calc. : C, 75·6; H, 5·9%). Lindemann (*loc. cit.*) gives m. p.'s 174° and 210°, respectively. On diazotisation in hydrochloric acid solution at the ordinary temperature (compare Morgan and Read, *loc. cit.*) and addition of an alkaline solution of β-naphthol, the deep red *9-methylcarbazole-3-azo-β-naphthol* separated. This compound was obtained from its solution in acetic acid in small, deep red needles, m. p. 212° (decomp.) (Found : C, 78·5; H, 5·2; N, 12·1. $C_{23}H_{17}ON_3$ requires C, 78·6; H, 4·9; N, 12·0%).

9-Methylcarbazole-3-arsinic Acid,  .—A suspension of 3-amino-9-methylcarbazole (19·6 g.) in a mixture of water (250 c.c.) and concentrated hydrochloric acid (25 c.c.) was cooled below 10° and diazotised with sodium nitrite solution. The diazo-solution was then cooled to 0° and neutralised with cold sodium hydroxide solution. The neutralised solution was added gradually with stirring at room temperature to a solution of sodium arsenite (arsenious oxide, 15 g.; sodium carbonate, 24 g.; water, 105 c.c.), to which 10 c.c. of a 10% solution of copper sulphate

previously treated with ammonia had been added. After the addition was complete, the mixture was stirred for 1 hour, boiled, and filtered from tarry matter. The filtrate on acidification deposited the crude acid (10·5 g.); this crystallised from glacial acetic acid in clusters of small, colourless needles, which did not melt below 300° (Found: As, 24·3. $C_{13}H_{12}O_3NAs$ requires As, 24·6%).

9-*Methylcarbazole*-3-*arsenious Chloride*.—A boiling solution of 9-methylcarbazole-3-arsinic acid (5 g.) in alcohol (20 c.c.) and concentrated hydrochloric acid (20 c.c.) containing a trace of iodine was saturated with sulphur dioxide for 10 minutes. On cooling, the crude *chloroarsine* separated as a gummy mass which gradually solidified. It was purified by dissolving it in benzene, adding light petroleum to the hot solution until all the colouring matter was precipitated, and then filtering and cooling it; the chloroarsine separated in small, colourless prisms, m. p. 121—122° (Found: As, 22·6. $C_{13}H_{10}NCl_2As$ requires As, 23·0%).

9-*Methylcarbazole*-3-*arsenious Oxide*.—A solution of the chloroarsine in acetone was treated with ammonia, and the mixture well shaken. The precipitate was filtered off, washed with water until free from chloride, and dried. The *oxide* is insoluble in the ordinary organic solvents. It has m. p. 182—185° (decomp.) (Found: As, 27·3. $C_{13}H_{10}ONAs$ requires As, 27·7%).—Guy's Hospital Medical School (University of London), S.E.1. [*Received, July 26th*, 1927.]

Derivatives of o-*Aminophenylarsinic Acid*. By Harold Burton and Charles Stanley Gibson.

During the course of investigations which have been carried out on heterocyclic arsenic compounds, a number of simple arsinic compounds have been prepared which might be useful to other investigators.

o-*Ethylaminophenylarsinic Acid*, $NHEt{\cdot}C_6H_4{\cdot}AsO(OH)_2$.—Ethyl sulphate (17 g.) was added to a constantly stirred solution of *o*-aminophenylarsinic acid (21·7 g.) in sodium hydroxide solution (45 c.c., 10%), heated on the water-bath, and the clear solution heated for 10 minutes after the initial reaction had finished. The red oil which separated on cooling solidified and was recrystallised from water, forming colourless needles, m. p. 128—129° (yield, 6 g.) (Found: As, 30·7. $C_8H_{12}O_3NAs$ requires As, 30·6%). The *nitroso*-derivative was prepared by adding a solution of sodium nitrite (2·5 g.) to a solution of the acid (2 g.) in dilute hydrochloric acid. The crystalline product (1·7 g.), which gave Liebermann's nitrosoamine-reaction, was recrystallised from water and obtained in colourless needles, m. p. 160° (decomp.) (Found: As, 27·0.

$C_8H_{11}O_4N_2As$ requires As, 27·35%). The *acetyl* derivative (m. p. 187—188°), prepared in the usual way, was readily soluble in water and in the common organic solvents; its *silver* salt was analysed and the acid shown to be dibasic (Found: Ag, 43·0. $C_{10}H_{12}O_4NAsAg_2$ requires Ag, 43·1%).

3-*Nitro*-6-*diethylaminophenylarsinic Acid*,

$$NEt_2 \cdot C_6H_3(NO_2) \cdot AsO(OH)_2.$$

—For the preparation of this acid we required 4-*nitro*-2-*aminodiethylaniline*. This was prepared by the ammonium sulphide reduction of 2 : 4-dinitrodiethylaniline, and the product isolated as the crystalline *hydrochloride*, yellow prisms, m. p. 205—206°. The *benzylidene* derivative formed yellow needles, m. p. 97—98°, from alcohol (Found: C, 68·4; H, 6·6. $C_{17}H_{19}O_2N_3$ requires C, 68·7; H, 6·4%). The base itself was obtained as a red, viscous oil. The hydrochloride was suspended in water, diazotised, and reduced with sodium stannite, giving *p*-nitrodiethylaniline, m. p. 75°.

A mixture of 4-nitro-2-aminodiethylaniline hydrochloride (24·5 g.), water (150 c.c.), and concentrated hydrochloric acid (25 c.c.) was diazotised at 0° with a sodium nitrite solution (7 g.; 20 c.c.). This diazo-solution was added to a stirred solution consisting of sodium arsenite (arsenious oxide, 15 g.; crystalline sodium carbonate, 65 g.; water, 105 c.c.; 5*N*-sodium hydroxide, 40 c.c.) and 10 c.c. of a 10% solution of copper sulphate which had been treated with an excess of ammonia. The mixture was stirred until frothing had subsided and then warmed until all effervescence had ceased. After cooling, it was stirred with decolorising charcoal, filtered, and the filtrate acidified with hydrochloric acid (Congo-red). The acid (5·5 g.) was filtered off and crystallised from a large volume of water, from which it separated in glistening, yellow needles, m. p. 195—196° (decomp.) (Found: As, 23·5. $C_{10}H_{15}O_5N_2As$ requires As, 23·6%).

3-*Nitro*-6-*diethylaminophenylarsenious Chloride*,

$$NEt_2 \cdot C_6H_3(NO_2) \cdot AsCl_2.$$

—3-Nitro-6-diethylaminophenylarsinic acid (3·2 g.), in alcohol (20 c.c.) and concentrated hydrochloric acid (10 c.c.) containing a trace of iodine, was saturated with sulphur dioxide for 30 minutes. On cooling, a yellow, crystalline product separated (3·0 g.); this crystallised from benzene in deep yellow prisms, m. p. 143—144° (Found: As, 22·1; Cl, 20·8. $C_{10}H_{13}O_2N_2Cl_2As$ requires As, 22·1; Cl, 20·9%).

When *o*-ethylaminophenylarsinic acid or its acetyl derivative was reduced under similar conditions, arsenic was eliminated from the molecule.—GUY'S HOSPITAL MEDICAL SCHOOL (UNIVERSITY OF LONDON), S.E.1. [*Received, July 26th,* 1927.]